



IBRACON 2008
50º Congresso Brasileiro do Concreto
September 5, 2008

RECENT ADVANCES IN CONCRETE AND APPLICATION OF NANOTECHNOLOGY

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**NORTHWESTERN
UNIVERSITY**

ACBM

Center for Advanced Cement-Based Materials



Congratulations to the Brazilian Concrete Congress on the 50th Session





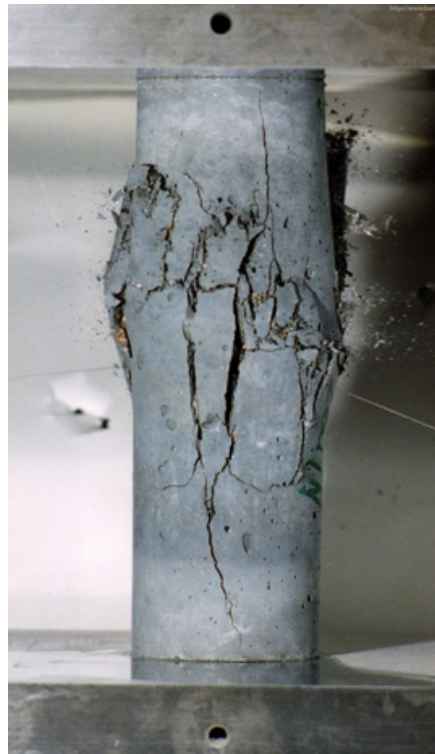
Contributing Researchers

- Liberato Ferrara, Politecnico di Milano
- Raissa Ferron, Northwestern University
- Amedeo Gregori, University of L'Aquila
- Seung Hee Kwon, Northwestern University
- Jean-Juste Mbele, Schlaumberger
- Paramita Mondal, Northwestern University
- Yon-Dong Park, Daegu Haany University
- Zhihui Sun, University of Louisville
- Nathan Tregger, Northwestern University
- Thomas Voigt, USG



High Strength Concrete

Maximizing compressive strength



Burj Dubai
“Dubai Tower”
> 800 m (1/2 mile)
[courtesy of wikipedia.org]



High Performance Concrete

Maximizing durability





Fresh State Properties

Flowability, compactibility

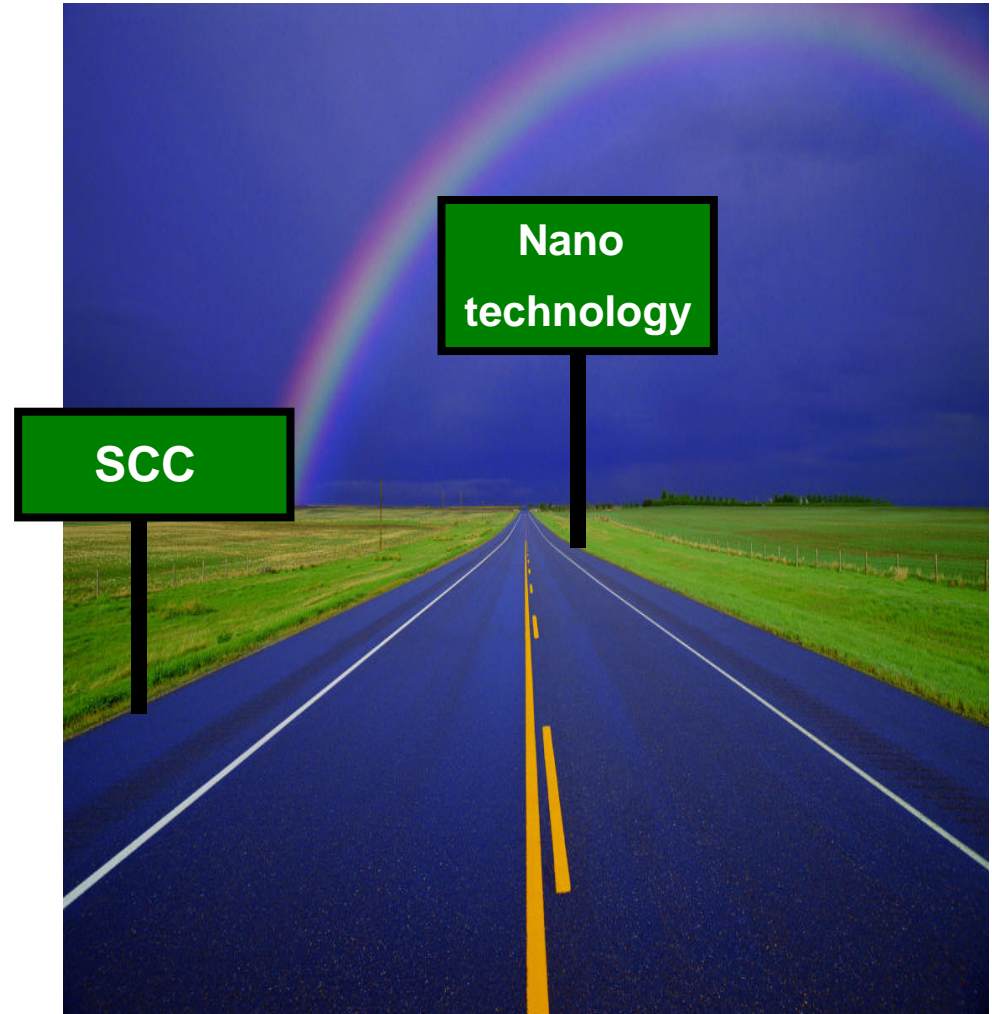




Presentation Roadmap

SCC

- Mix design model
- Segregation (Fiber)
- Formwork Pressure
- Structural Buildup
- Slip-Form Paving
- From lab to practice



Nanotechnology



Self-Consolidating Concrete

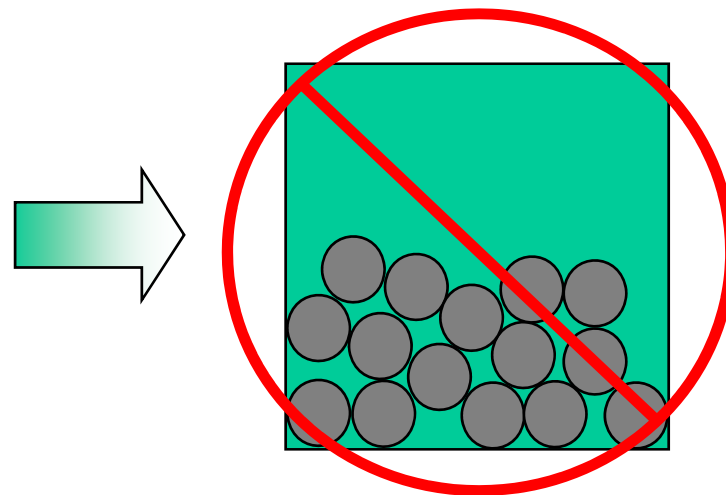
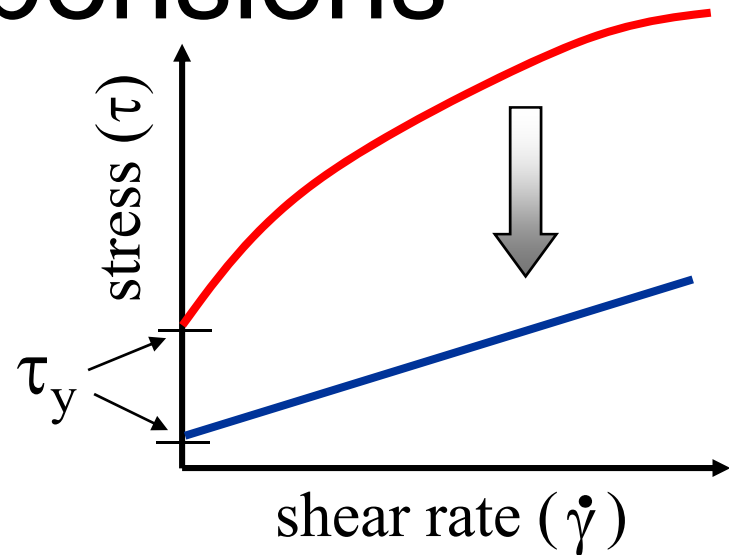
- Movie:





Conditions for Self-Flowing Suspensions

- Low stress required to initiate flow:
⇒ low yield stress (τ_y)
- Low stress required for continuous deformation
⇒ low viscosity $\left(\eta = \frac{\tau}{\dot{\gamma}} \right)$
- Rheology of the matrix must be controlled to avoid particle segregation (i.e. coarse aggregates)





HAAKE-RS150 Rheometer





Influence of Yield Stress

- Yield stress measured using the vane configuration:



2.7 Pa



25.5 Pa



31.9 Pa

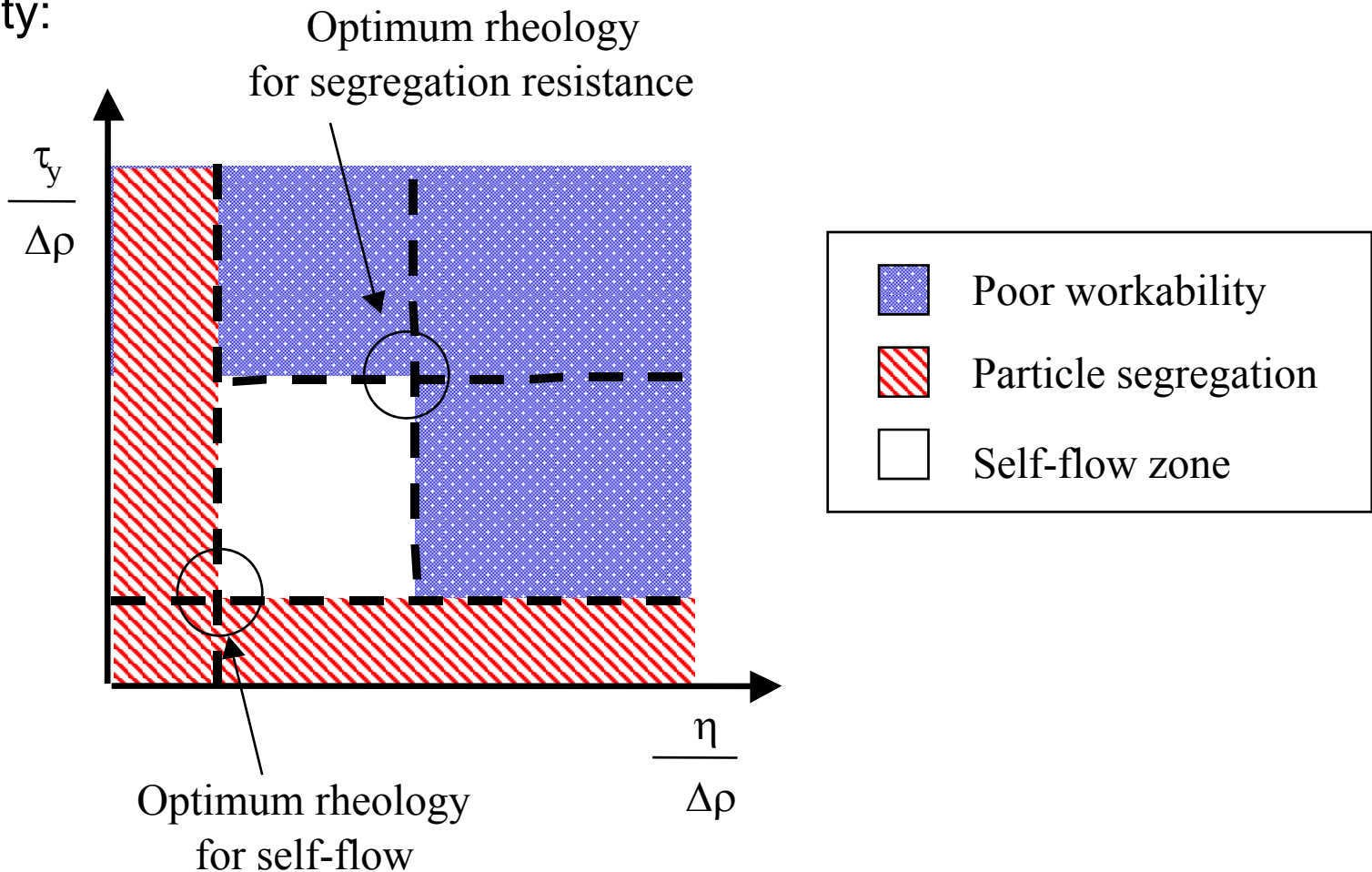


141.9 Pa



Self-flow Zone Concept

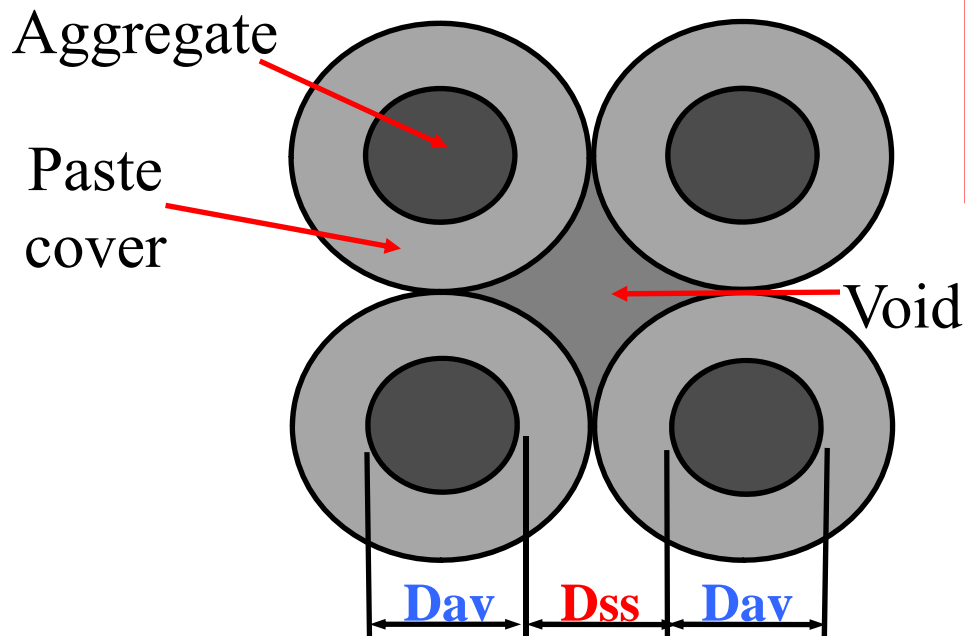
- Matrix yield stress and viscosity must be optimized for self-flowing capability:





Minimum Paste Model

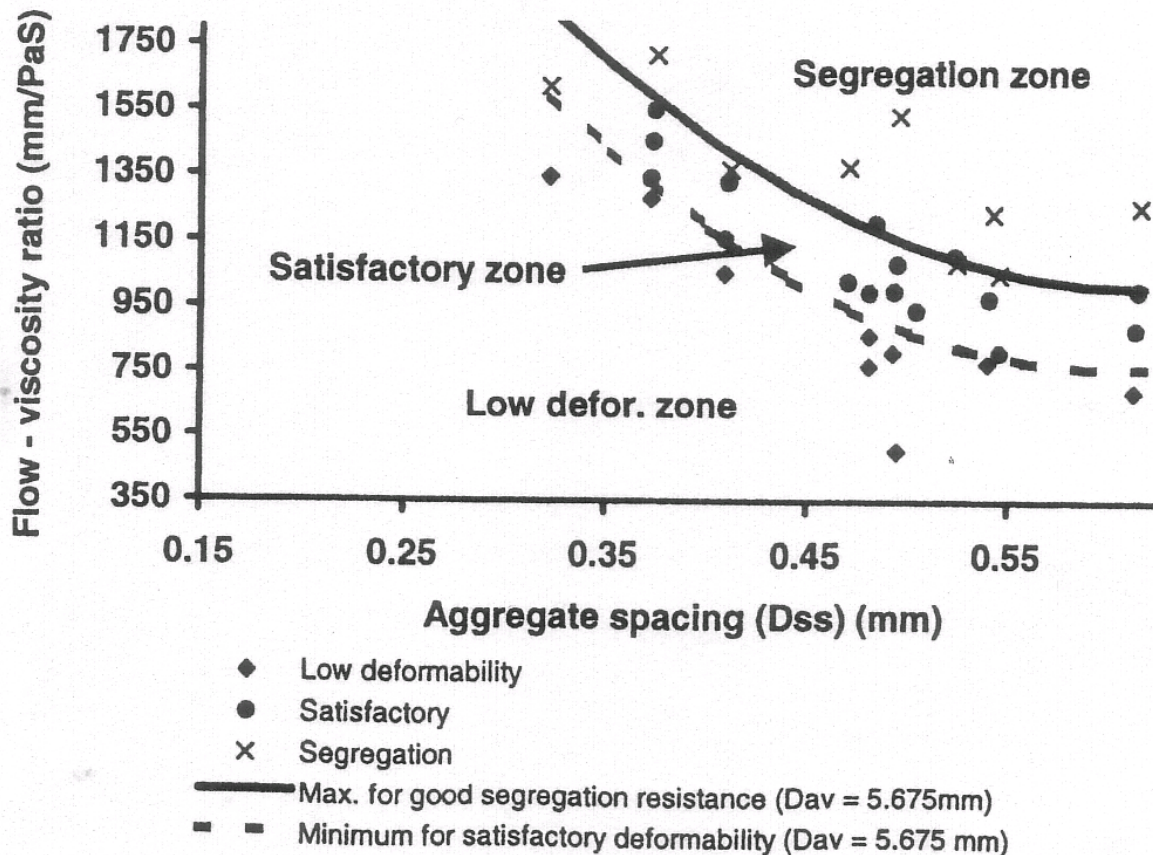
- Minimum Paste Model: accounts for aggregate interaction
 - Min. paste volume needed in to fill voids and coat aggregates
 - Concrete performance predicted through paste matrix
 - Required paste rheology depends on average aggregate spacing (D_{ss}), average aggregate diameter (D_{av}), and density difference between aggregate and paste.



D_{ss} is a function of the void content, average diameter, and aggregate volume (paste volume).



Minimum Paste Model: Self-flow Zone



- *Min. flow and Min. viscosity for good performing SCC*
- *Viscosity and paste flow can not be varied independently*

Model is characterized by:

- Min. flow
- Min. apparent viscosity
- Optimum flow/viscosity ratio

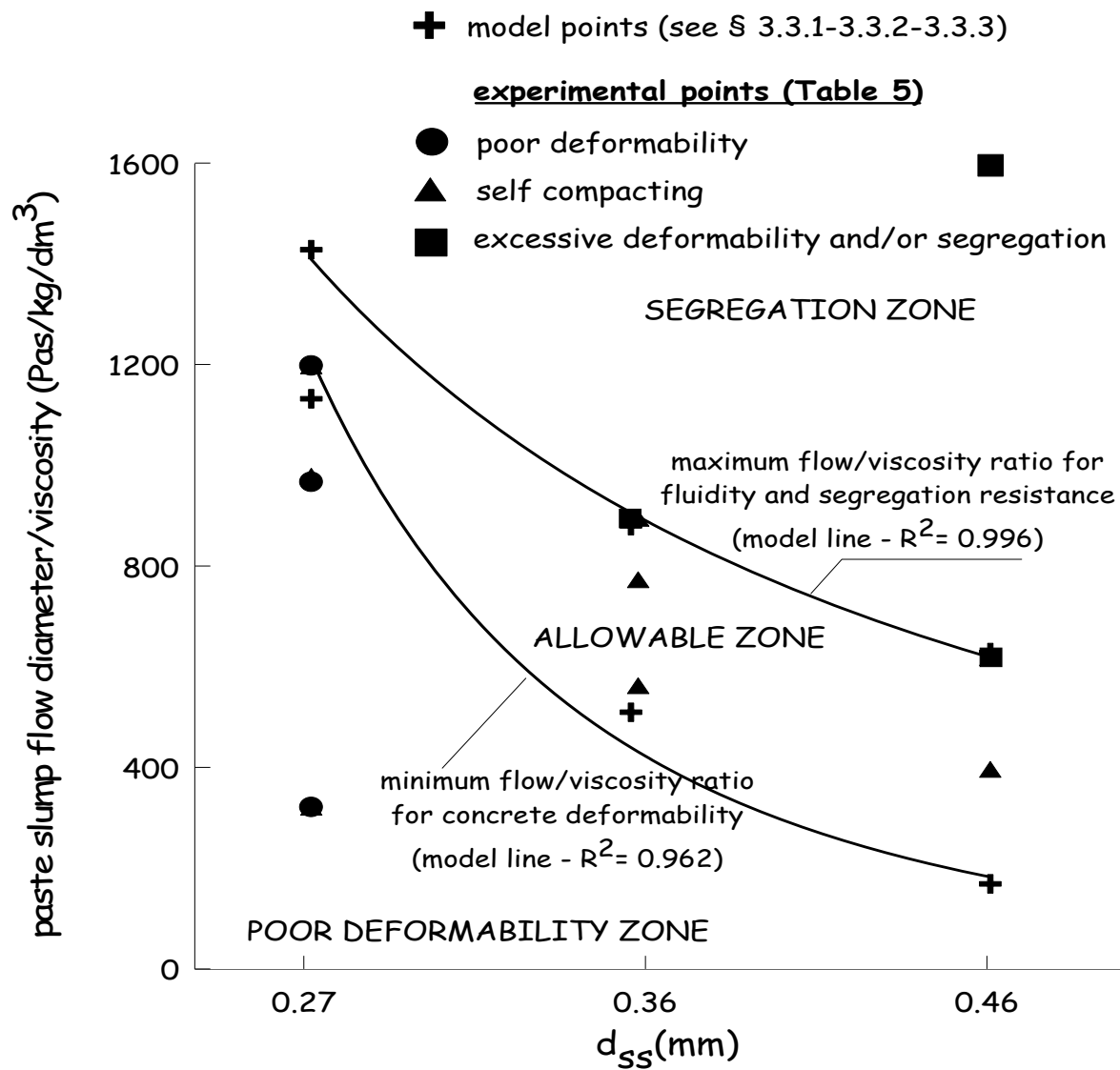


Application of minimum paste model to self-consolidating fiber reinforced concrete (SCFRC)





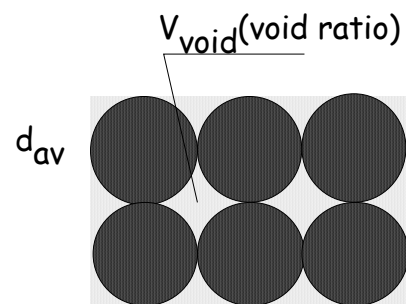
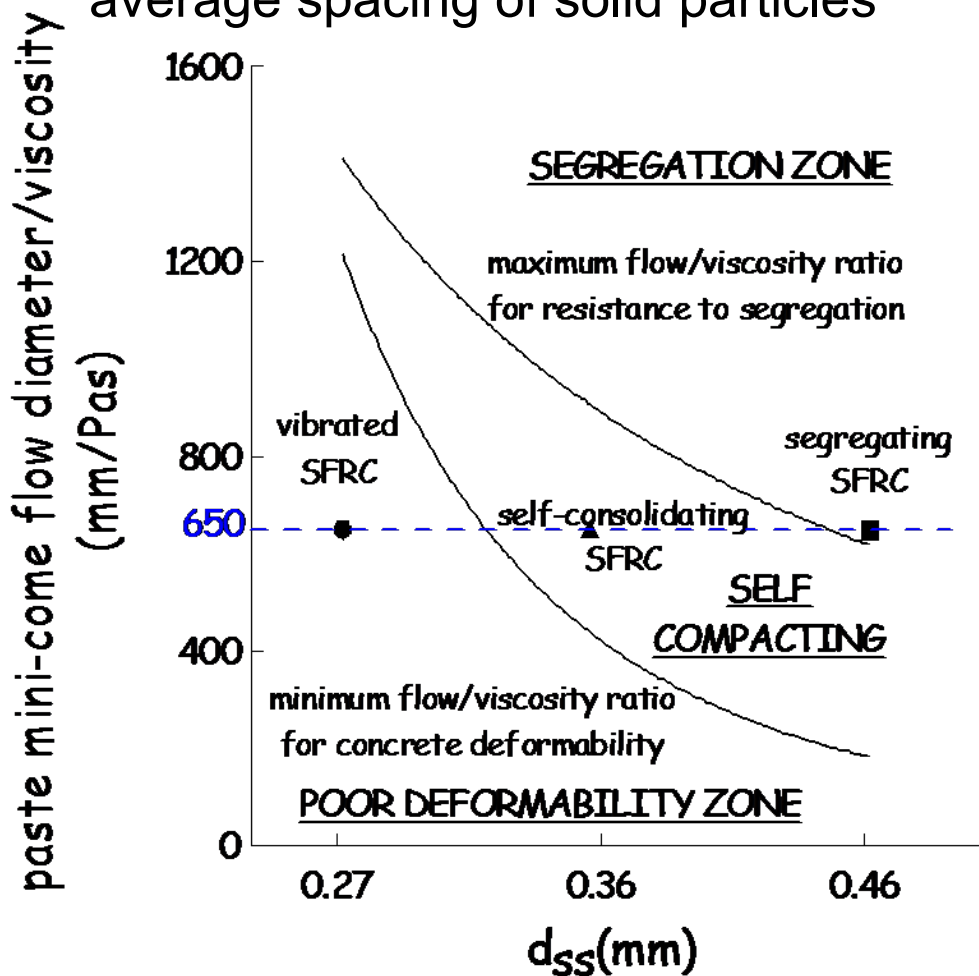
Self-flow Zone for SCFRC



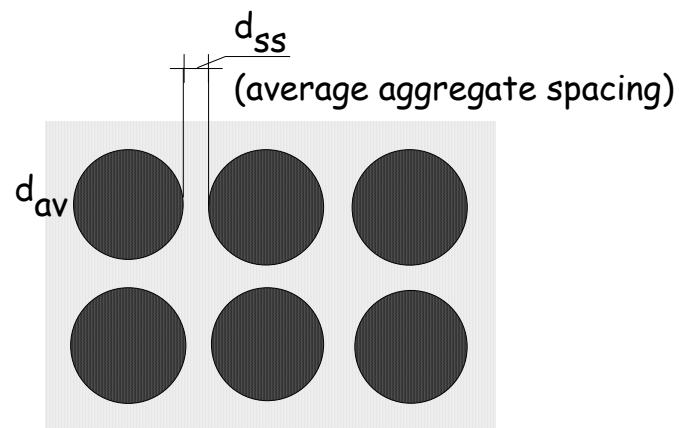


Mix design

- Optimum flow-viscosity ratio of suspending cement paste vs. the average spacing of solid particles



$$V_{paste} = V_{void}$$



$$V_{paste} > V_{void}$$

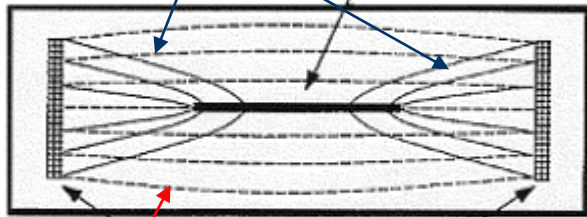


Non-destructive monitoring of fiber dispersion: Alternate Current Impedance Spectroscopy (AC-IS)

Current lines under high frequencies AC

Fibers act conductive

Submerged fiber



Electrodes

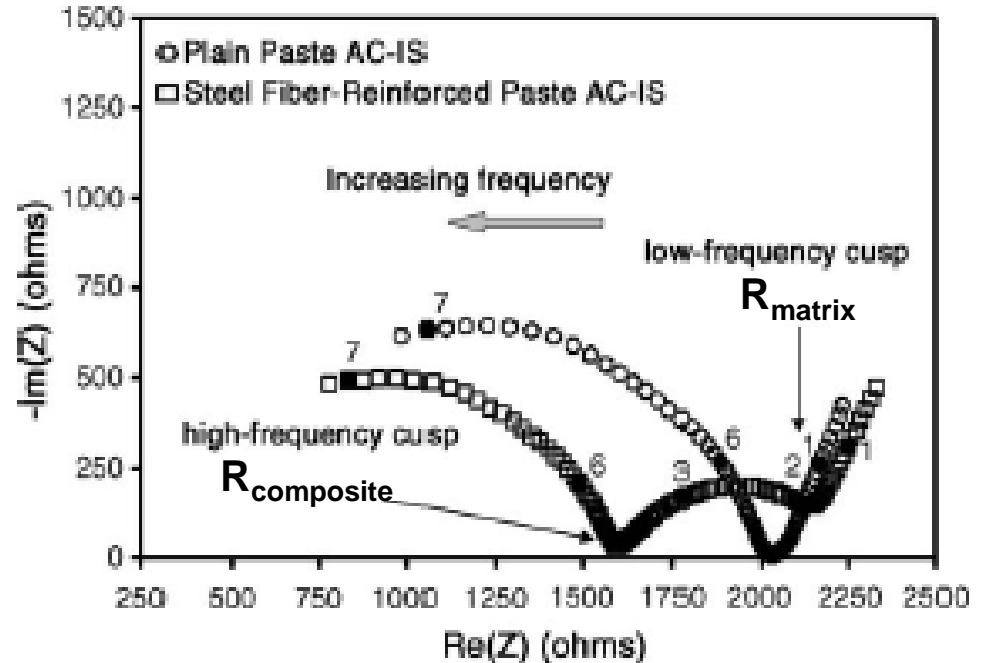
Current lines under low frequencies AC

Fibers act insulating

**MATRIX NORMALIZED
CONDUCTIVITY**

$$\frac{R_m}{R} = \frac{\sigma}{\sigma_m} = 1 + [\sigma]_{fibers} V_{fibers}$$

$$[\sigma]_{fibers} = \frac{1}{3} \left[\frac{2(AR)^2}{3 \ln(4AR) - 7} + 4 \right]$$



dual arc behavior

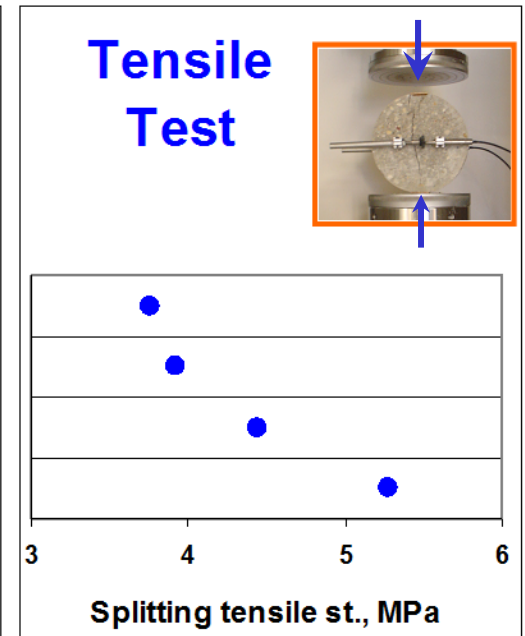
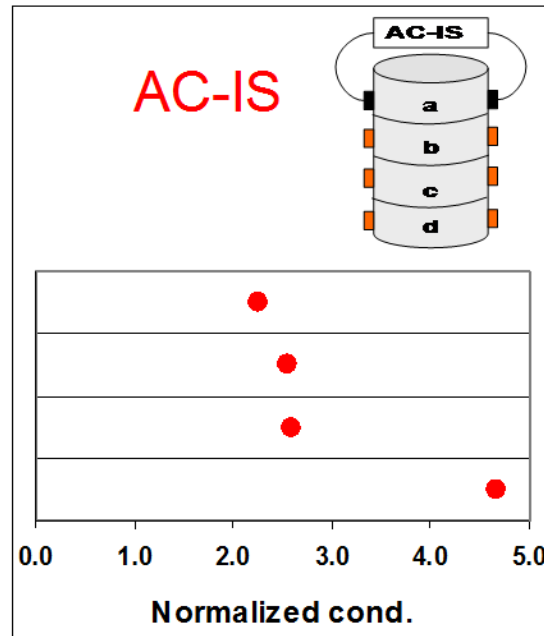
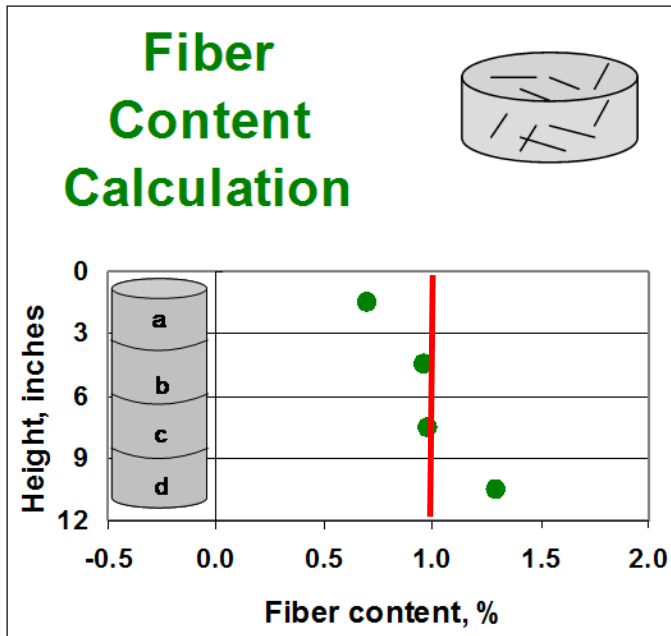
Low frequency cusp R_{matrix} : matrix resistance

High frequency cusp $R_{composite}$:
fiber reinforced composite resistance



Fiber Segregation

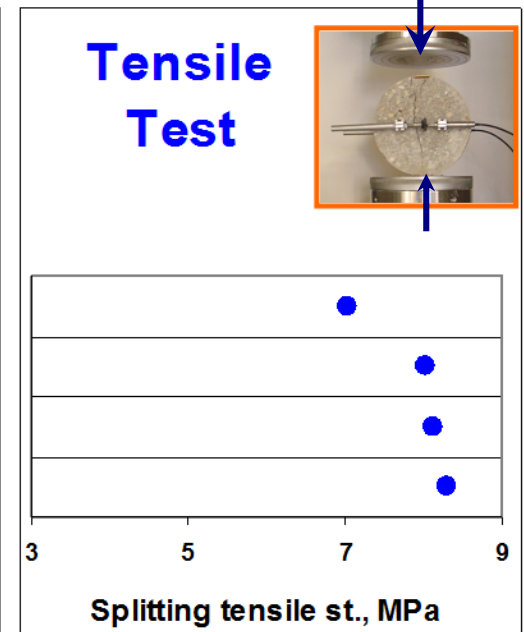
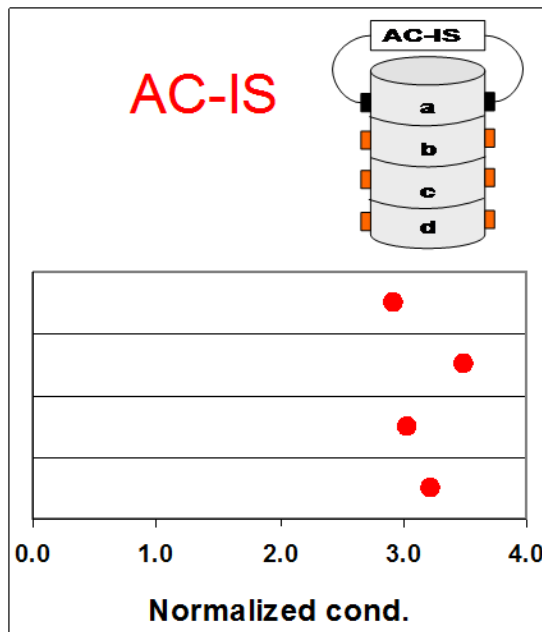
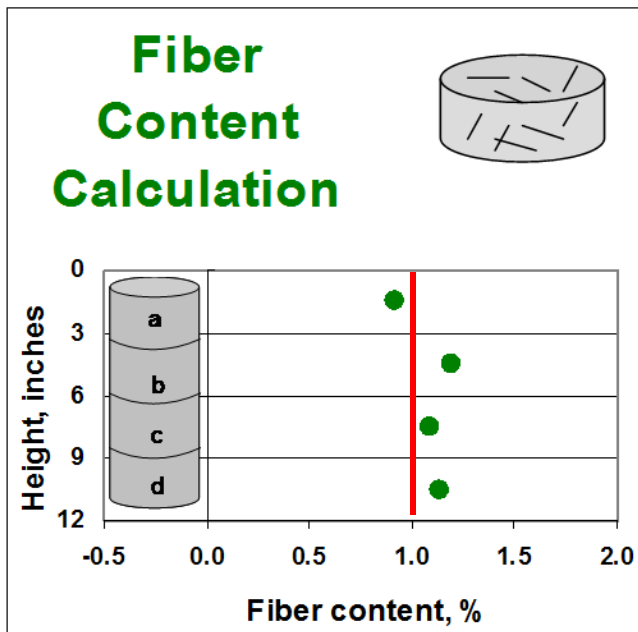
- Conventional concrete:
 - 40 mm fibers, 1 % vol.
 - 2 min. vibration





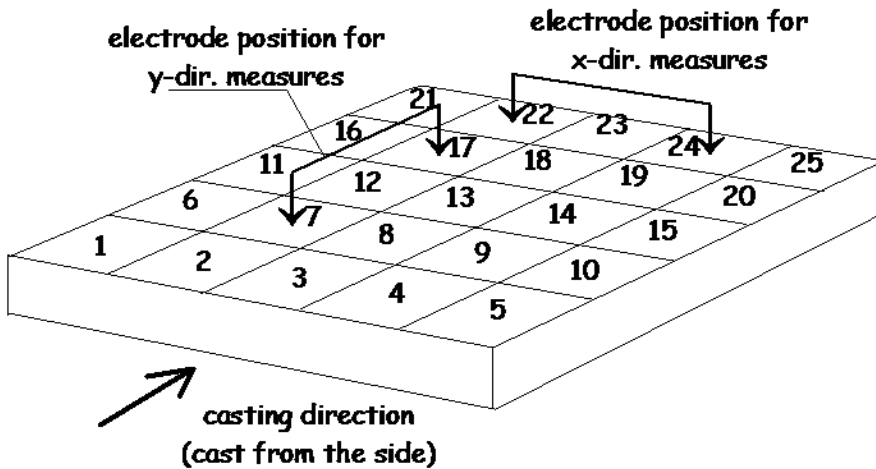
Fiber Segregation

- Self Consolidating Concrete
 - 40 mm steel fibers,
 - 1 % vol.





Non-destructive monitoring of fiber dispersion: Alternate Current Impedance Spectroscopy (AC-IS)

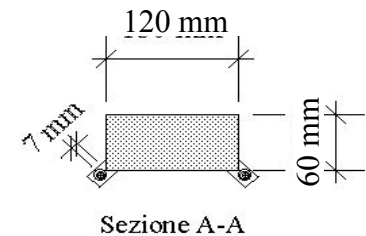
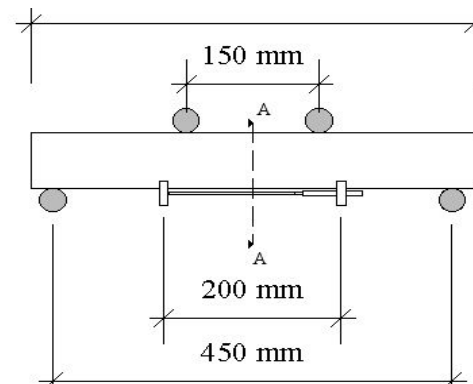
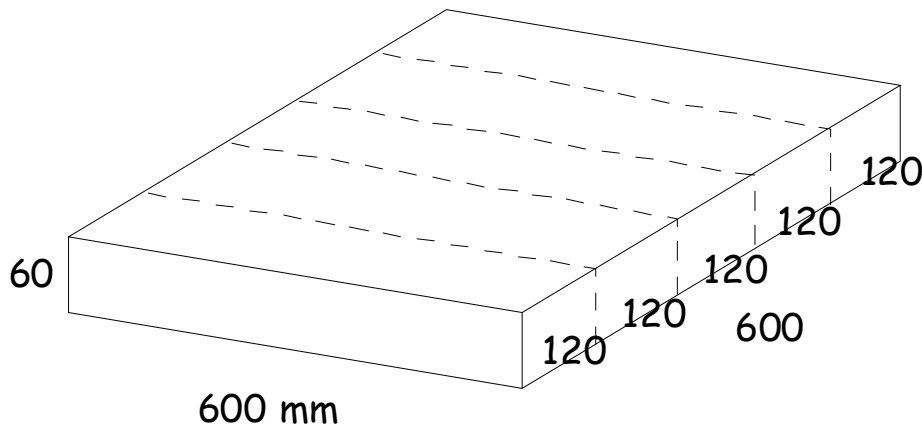


Vibrated SFRC

Self Consolidating SFRC

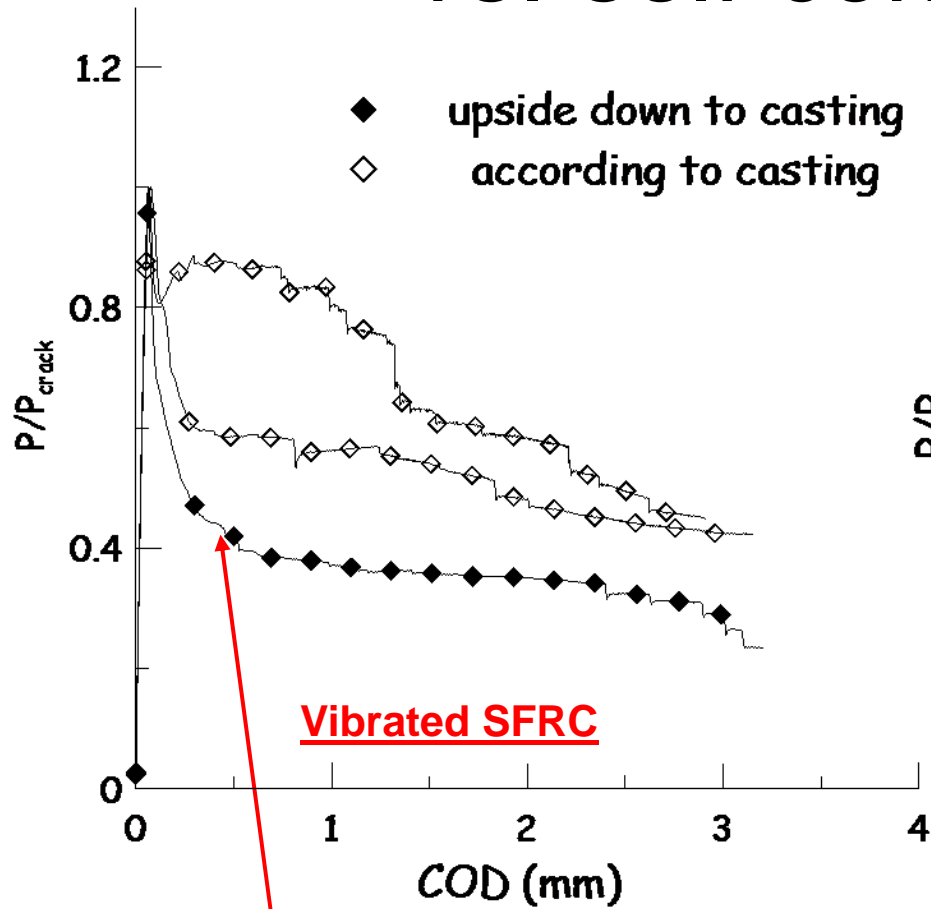
Segregating SFRC

After AC-IS measurements cut beams from the plates and test in 4 point bending

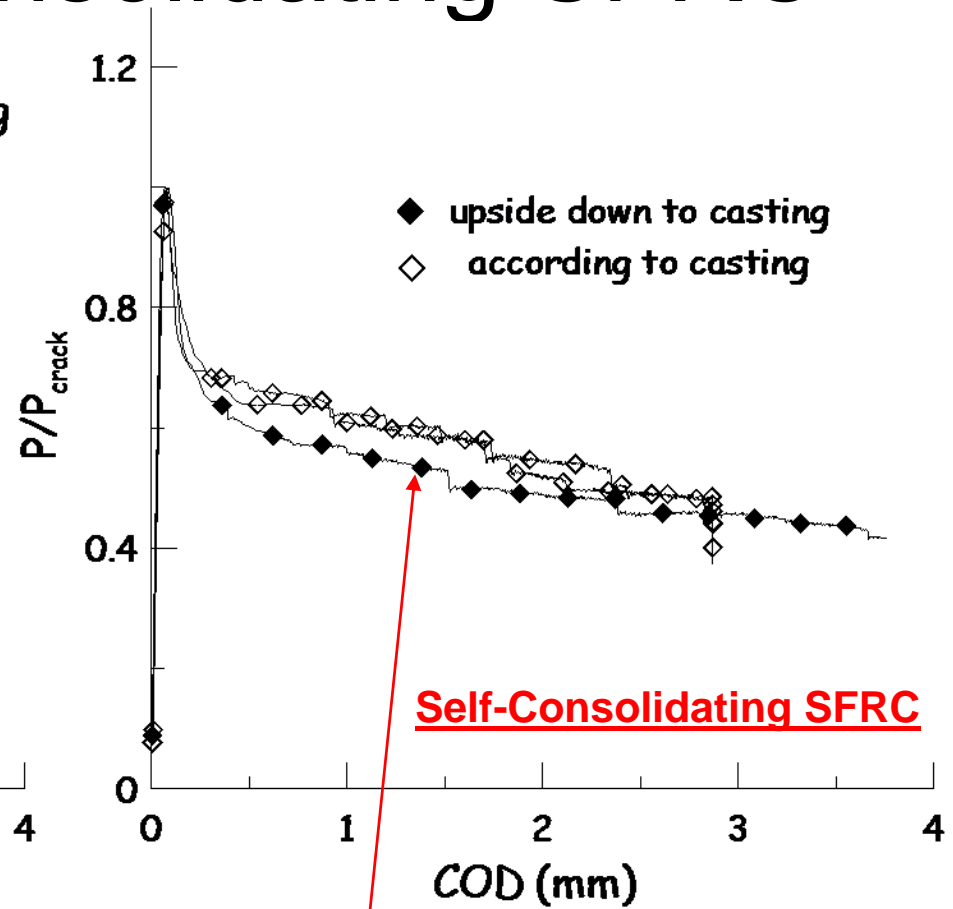




Four-point bending: vibrated vs. self consolidating SFRC



High scattering for companion specimens
(cut from the same slab)



Low scattering for companion specimens
(cut from the same slab)



Casting with SCC

One advantage of SCC is increase in construction due to higher casting (rates can exceed 100 m/h).

However,  Casting Rate  Formwork pressure



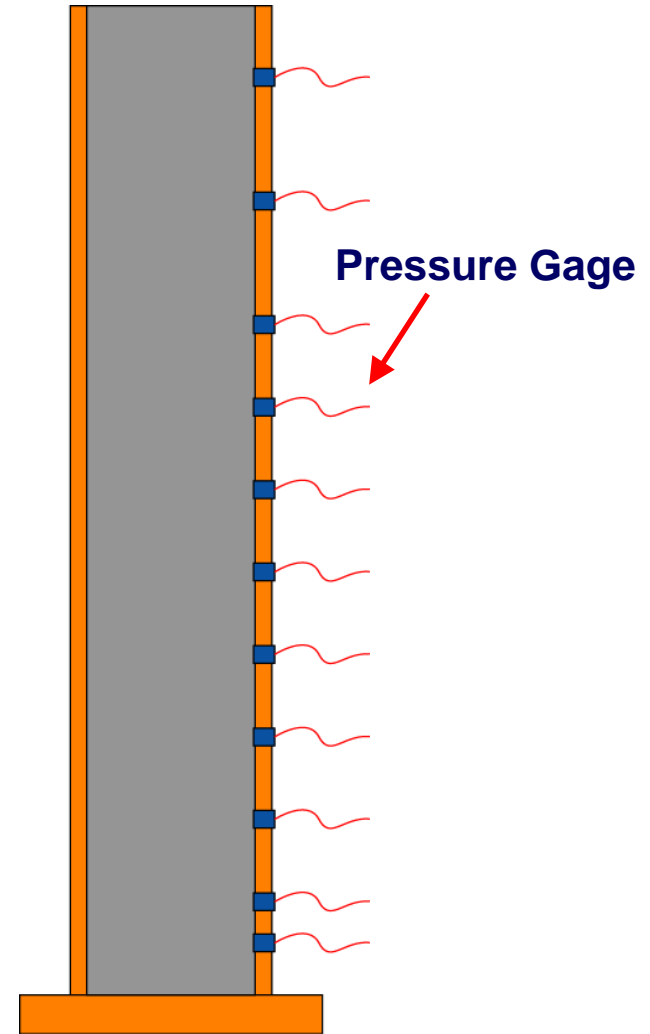
- Therefore, SCC formworks are typically designed for hydraulic pressures.



SCC Formwork Mock-up Test



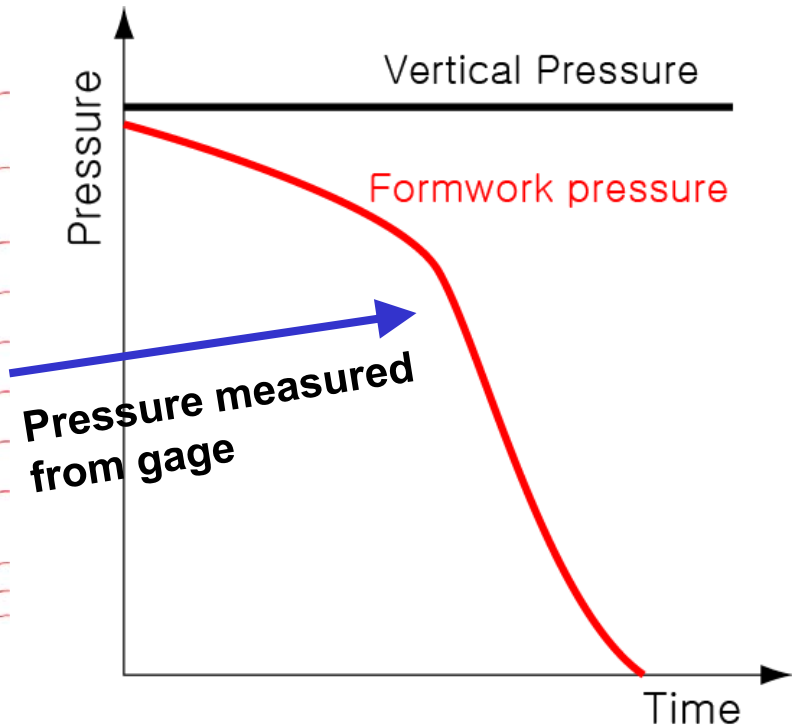
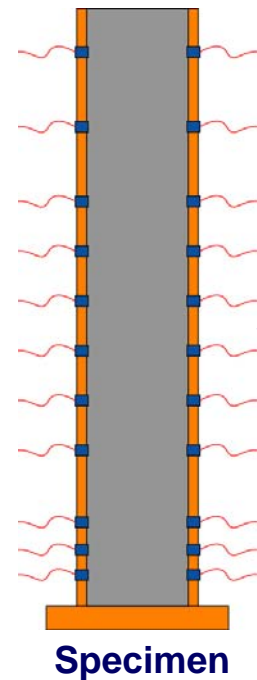
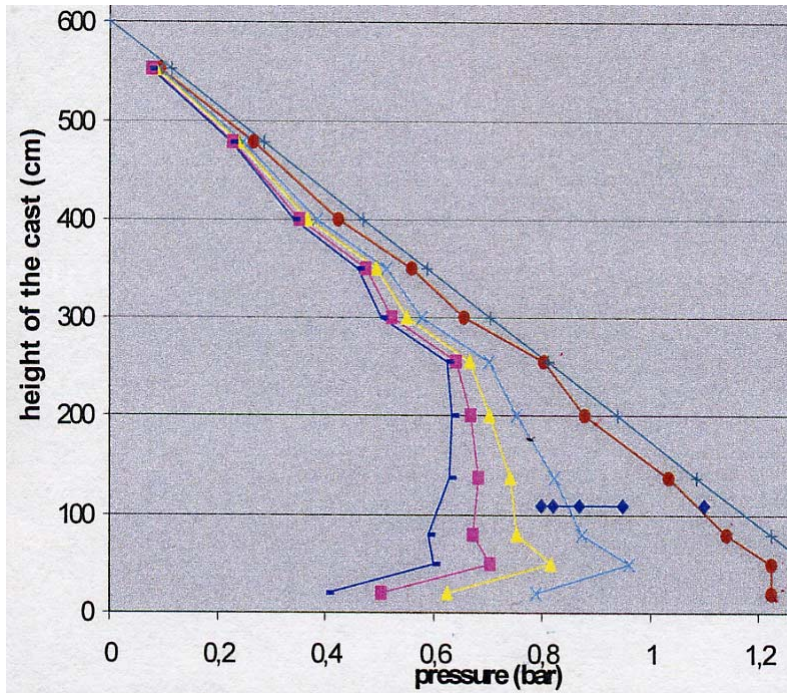
Mock Up Test (2007, Dante Galeota, and et al.)



Specimen



Pressure Profile



Mock Up Test (2007, Dante Galeota, and et al.)



Research Program

Goal

Reduction of the formwork pressure

- Reduce the initial formwork pressure
- Decrease the cancellation time of formwork pressure

Research Branch

Understanding of Fundamental Mechanisms

- Develop protocol to evaluate structural rebuilding
- Understand effect of material constituents on rheology and flocculation
- Simulation of flow behavior

Application in Practice

- Development of test method and laboratory test apparatus
- Development of prediction model for formwork pressure



Laboratory Setup for Formwork Pressure Measurement

- Simulation range: Real scale column heights up to 20 m, and casting rates ranging from 0 m/hr to 25m/hr

Lab formwork

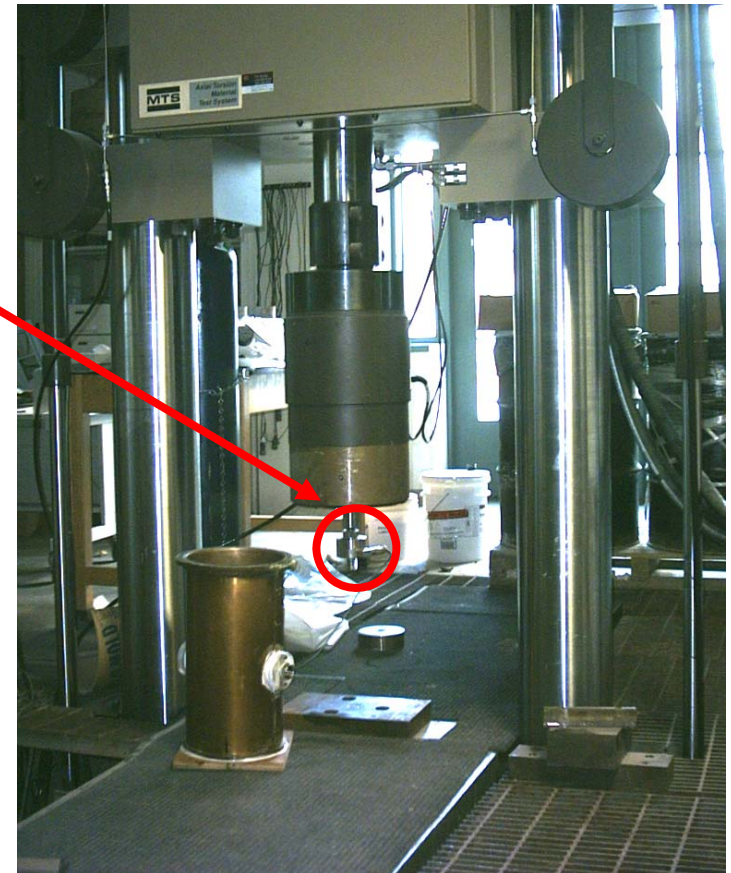
(V~20 Liter, H= 45cm, D=23 cm)



Loading Cell

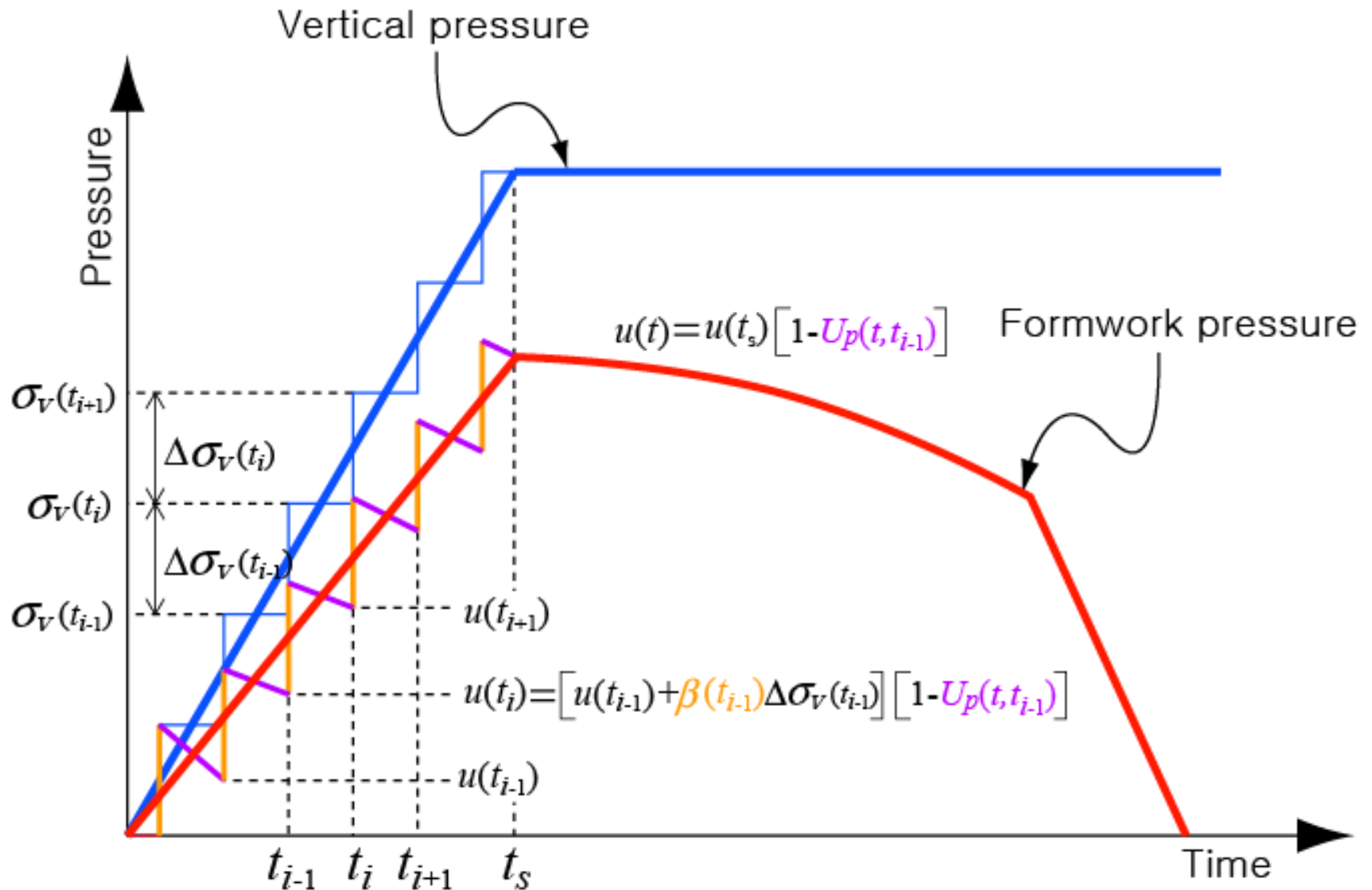


Pressure Sensors
(capacity: 50psi = 344kPa)





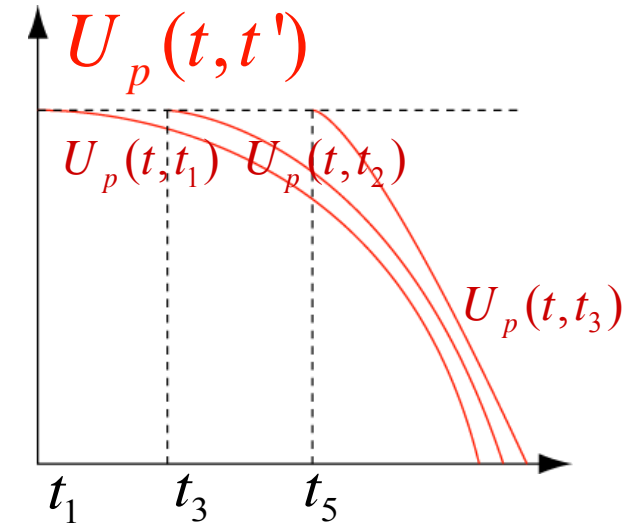
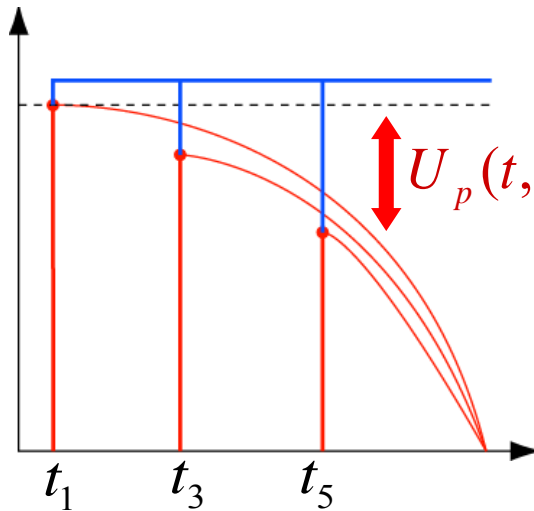
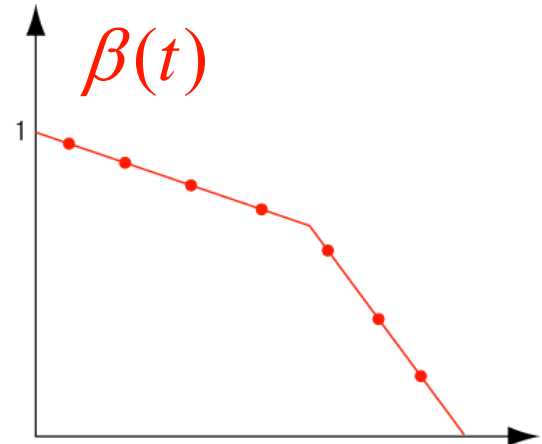
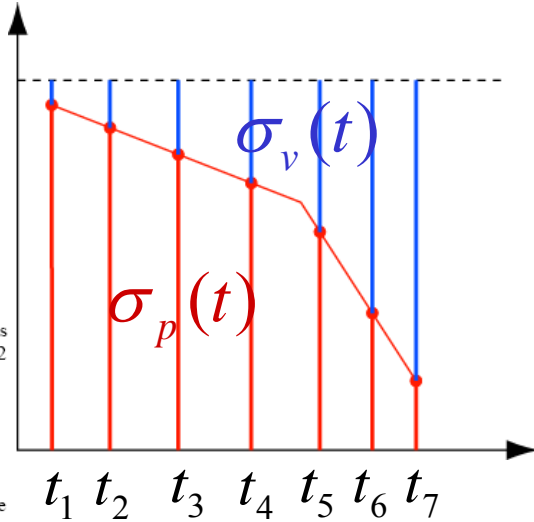
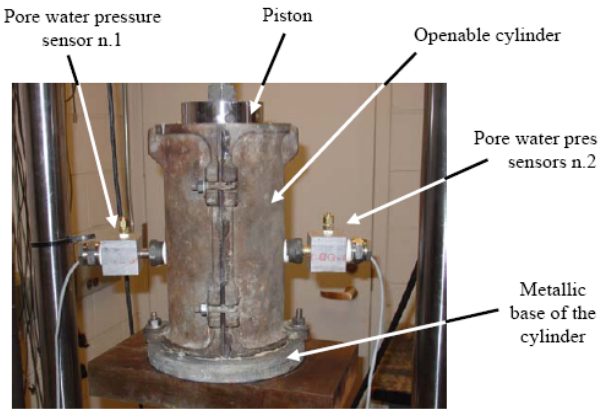
Prediction of Formwork Pressure





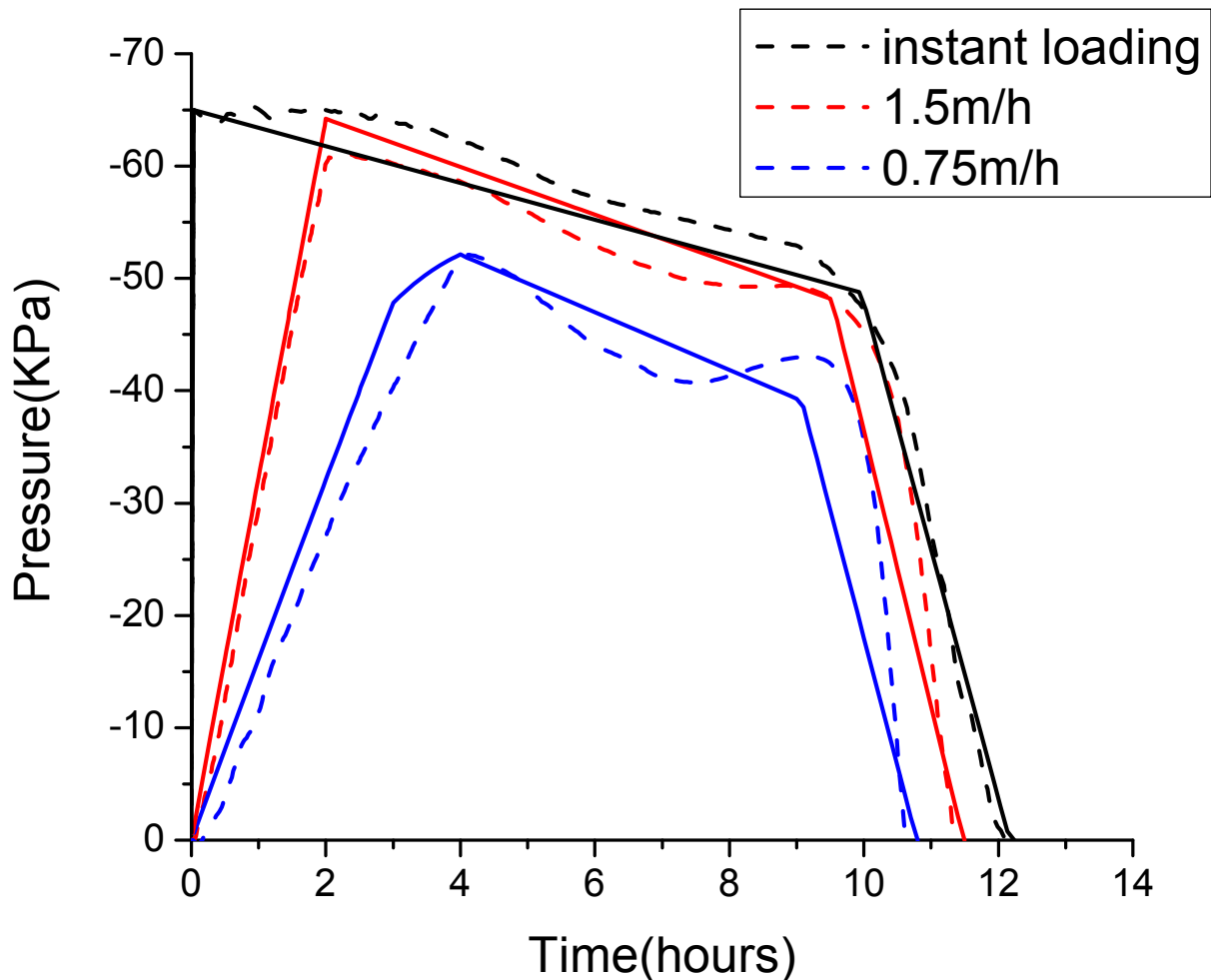
Tests to Find $U_p(t, t')$ and $\beta(t)$

$\beta(t)$ $U_p(t, t')$



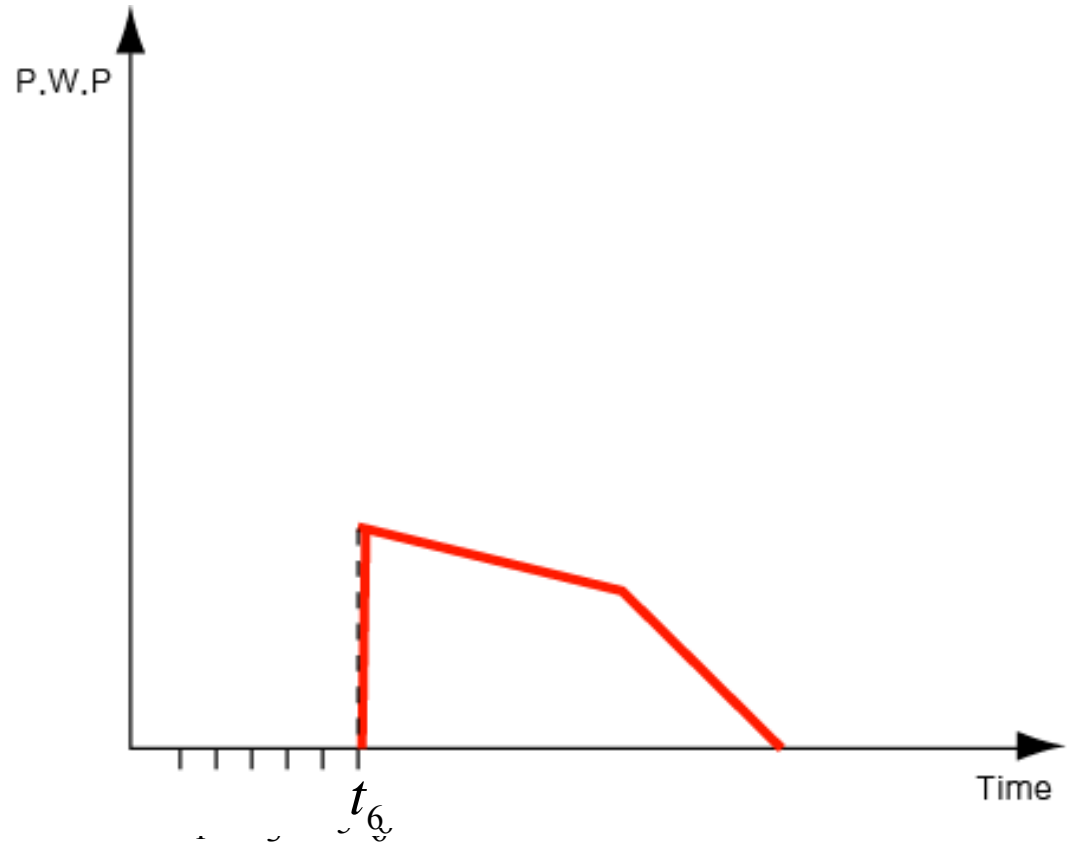
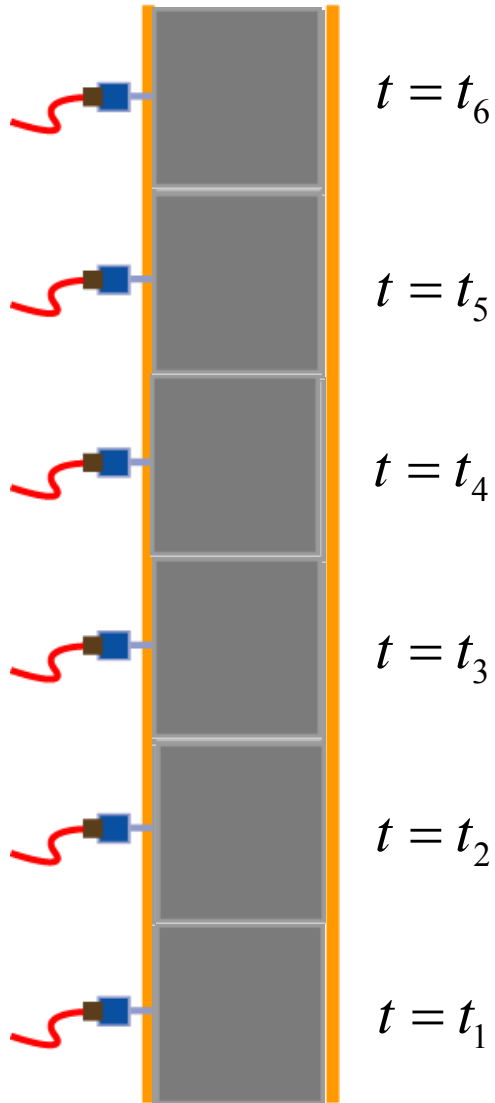


Calculation of Formwork Pressure Based on New Assumption



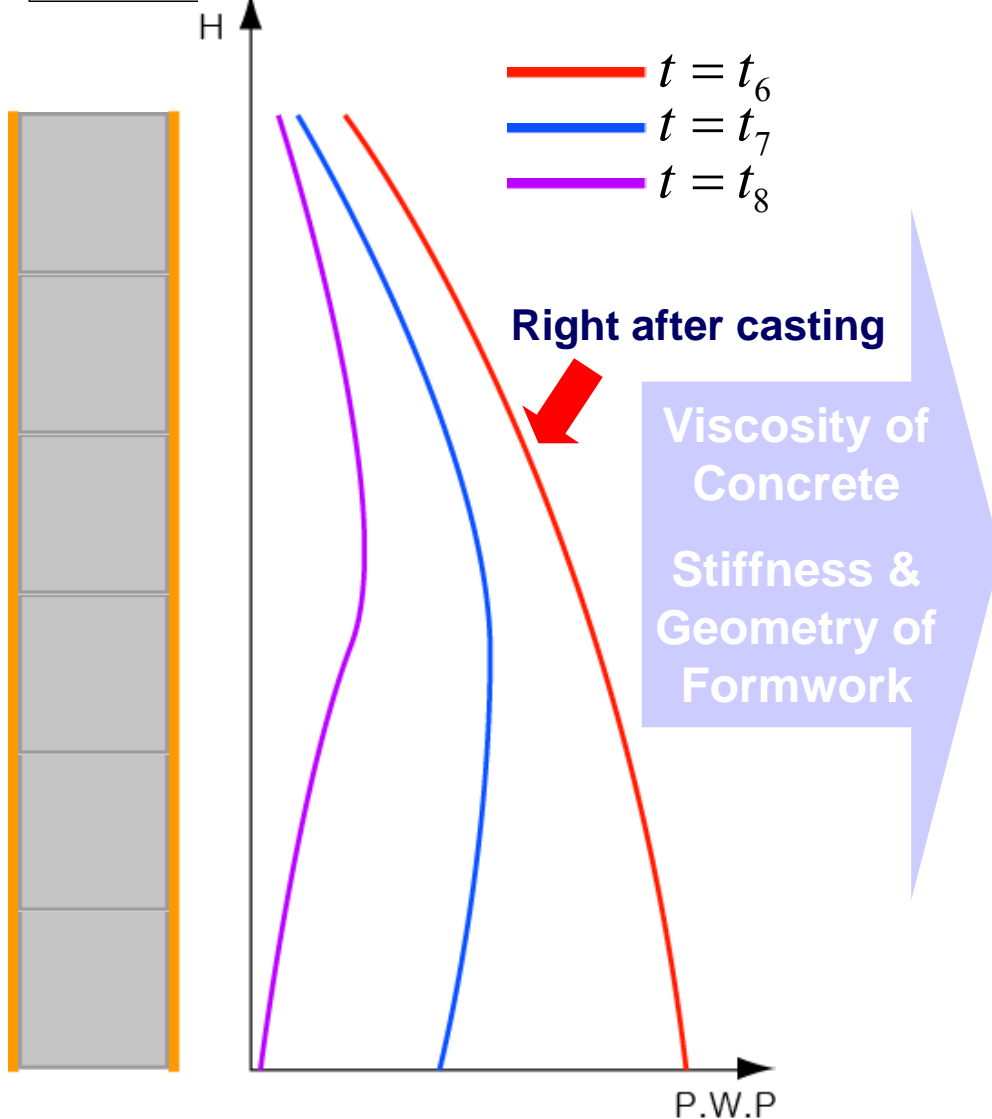


Calculation of Formwork Pressure

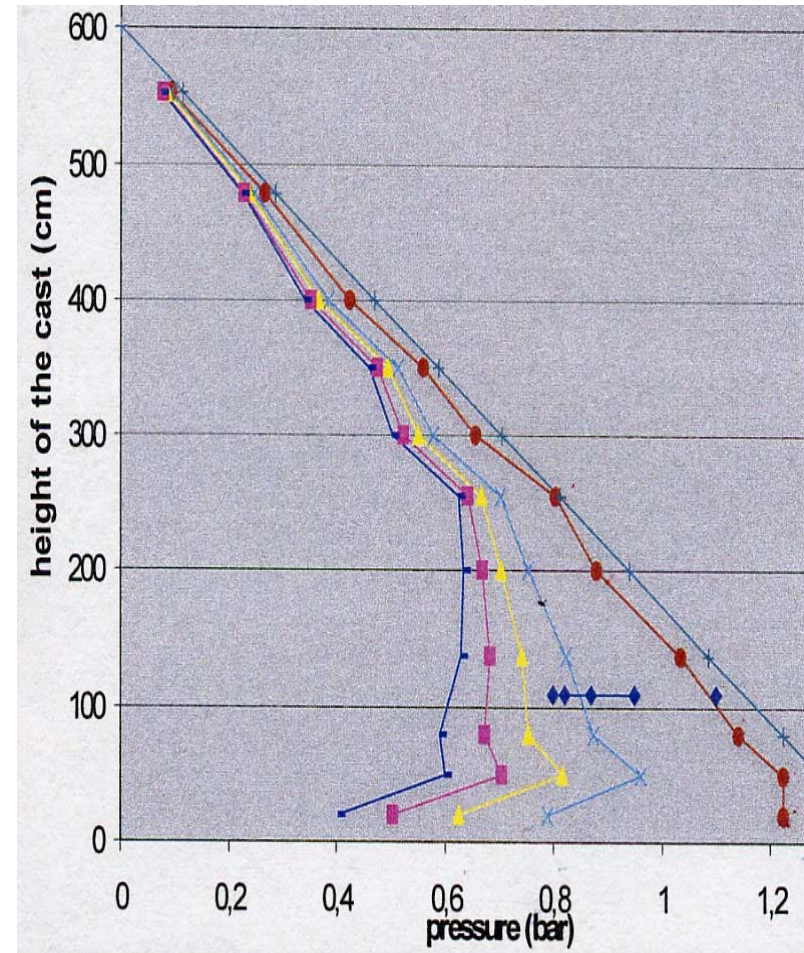




Calculation of Formwork Pressure



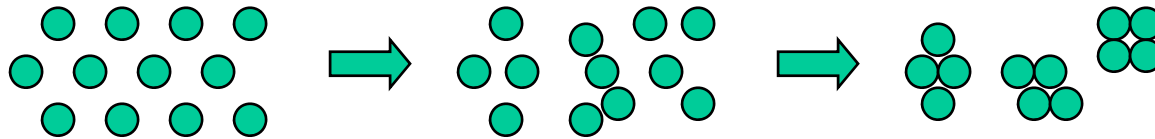
Mock Up Test
(2007, Dante Galeota, and et al.)





Flocculation: Aggregation of Colloidal Particles

Flocculation is the formation of flocs within a liquid/solid suspension



Where is flocculation important? Why is flocculation important?



Paints



Extruded Ceramics



Emulsions

Flocculation is involved in a wide variety of applications!



Applications to Cement

- Self consolidating concrete (SCC)
 - Requires stable suspension in order to provide workability
- Extrusion
 - Requires workability but also fast rebuilding upon processing
- Improving the slipform paving process
 - Combination of both

Zhen 2006

GOMACO



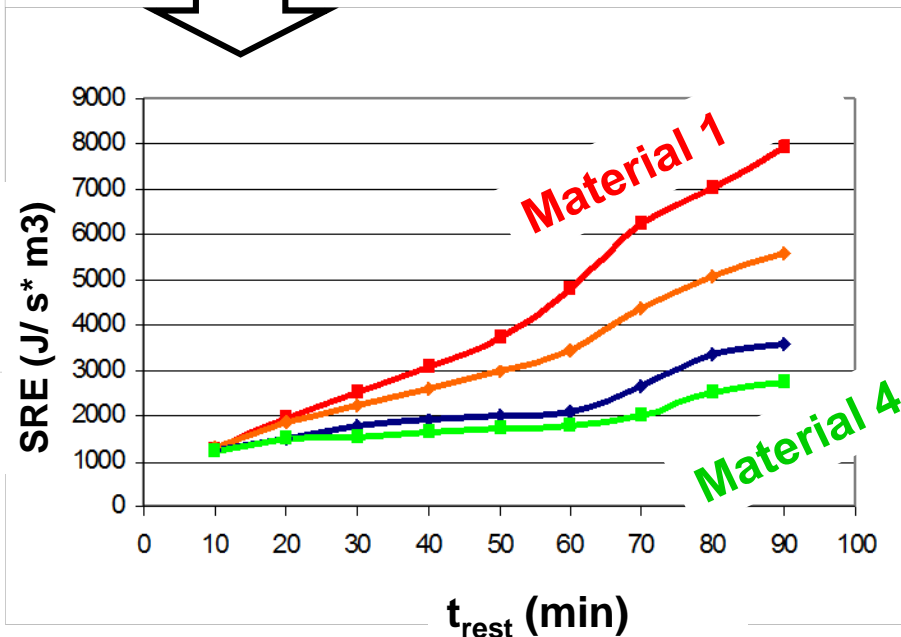
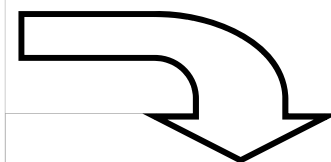
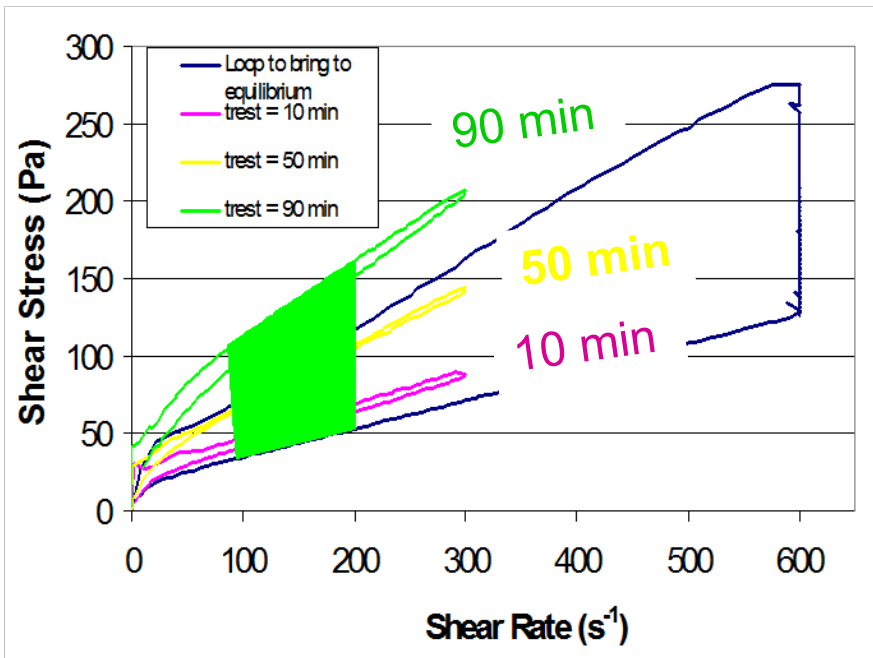


Structural Build-up of Cementitious Materials

- Irreversible
 - Hydration mechanisms
- Reversible
 - Thixotropy: time dependent change in viscosity
 - Particle flocculation (zeta potential, changes in chemistry, etc)
- *How to measure structural build-up during dormant period?*
- Hydration
- Rheology
- Imaging
- Particle size evolution
- Changes in chemistry



Rheological Protocol to Measure Structural Rebuilding



Slope ,

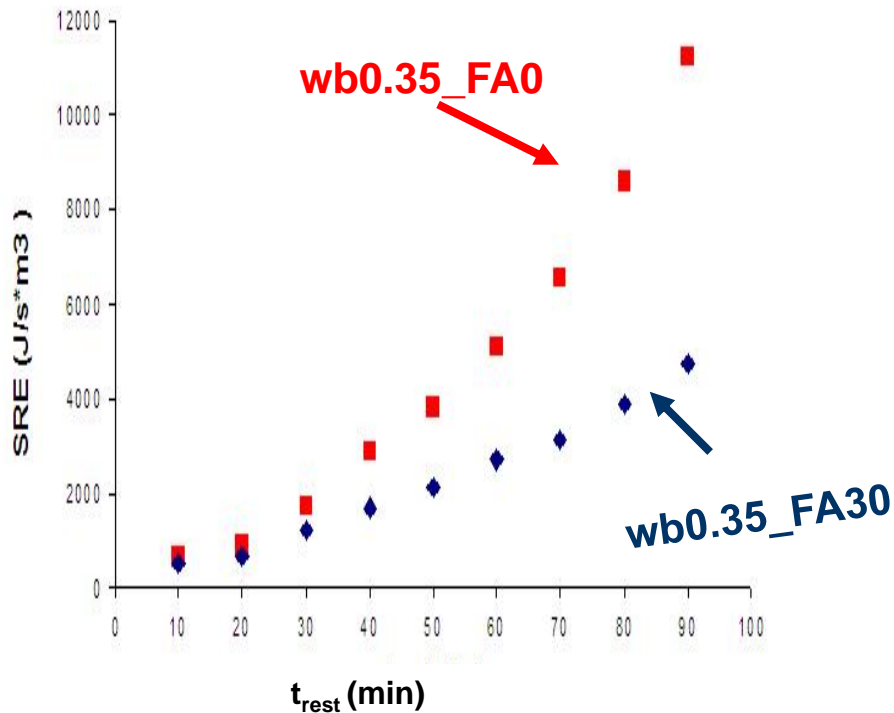


Rate of Rebuilding



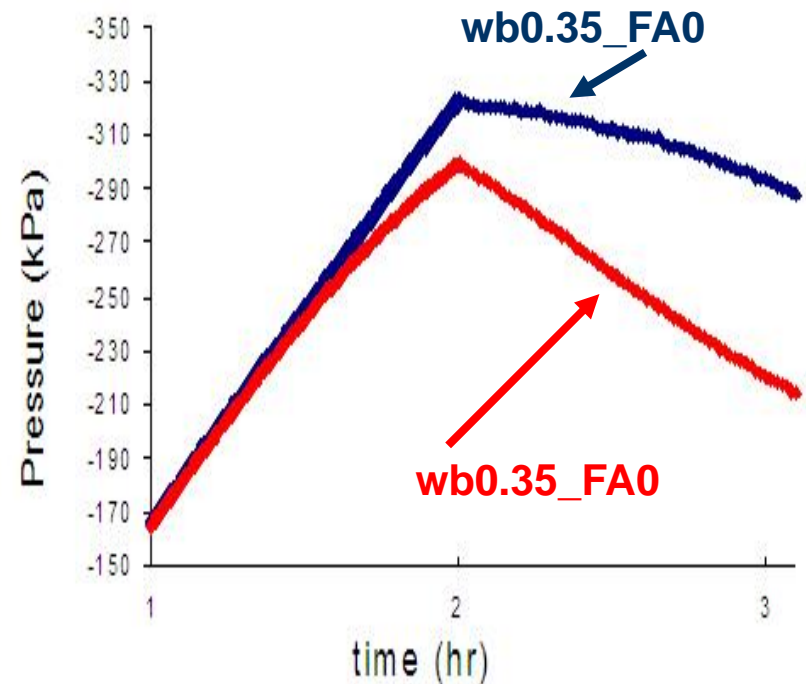
Relating Rebuilding and Formwork Pressure

- Structural Rebuilding of cement paste:



Flow diameter = 33 cm

- Formwork pressure simulation of cement paste (H = 14m, R = 7m/hr)



Flow diameter = 33 cm

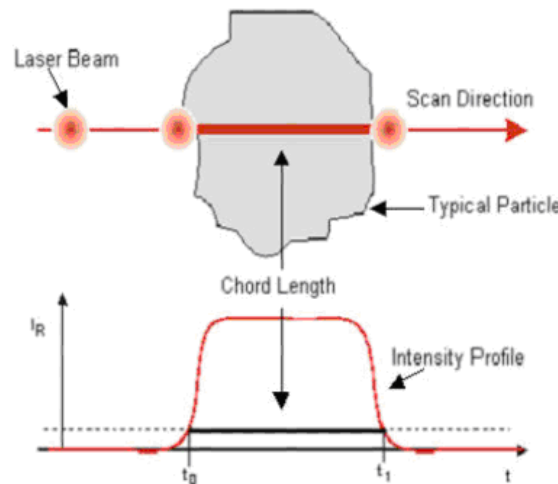
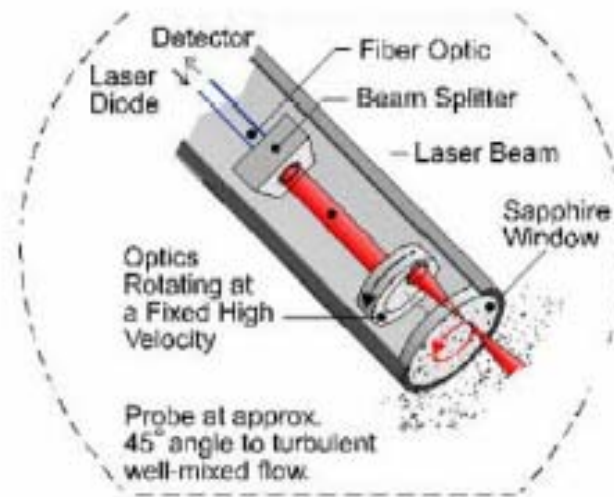


FBRM: A Way to Measure Floc Size

Focus Beam Reflectance Measurement (FBRM):

Gives information about Floc size → indirect indication of flocculation

- *in situ*/in-line information about the evolution and size of particle
- scans highly focused laser beam across suspension and measure time duration of back scattered light



- Time taken for beam to scan is measure of particle size
- Focus beam cross particle on a straight line between any 2 points.
- Hundreds of thousands of chords are measured per second
- Chord length range: 0.5 – 1000 μm

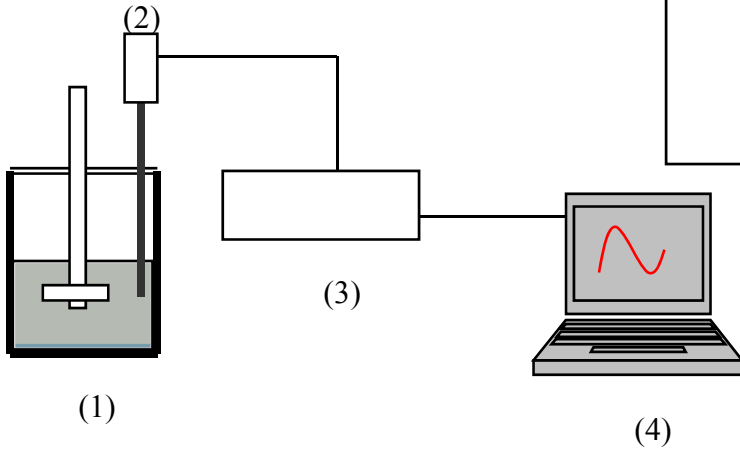
(Mettler-Toledo, 2005)



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FBRM Set-up

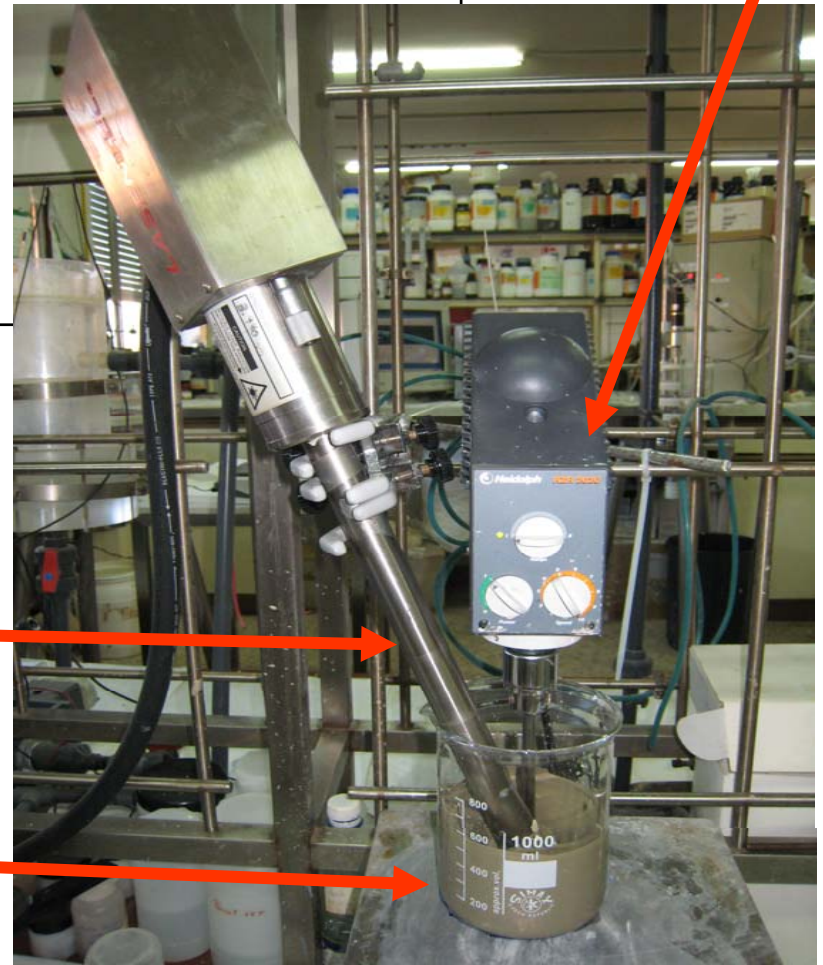
- (1) Mixing vessel
- (2) FBRM probe
- (3) Processing unit
- (4) PC for data logging and analysis



Agitator

FBRM
PROBE

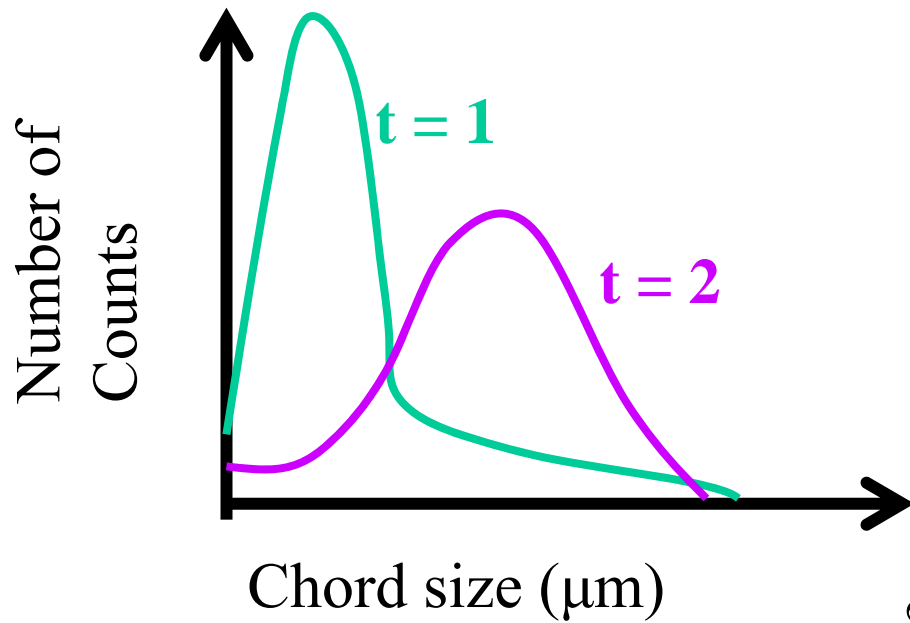
400 ml Sample



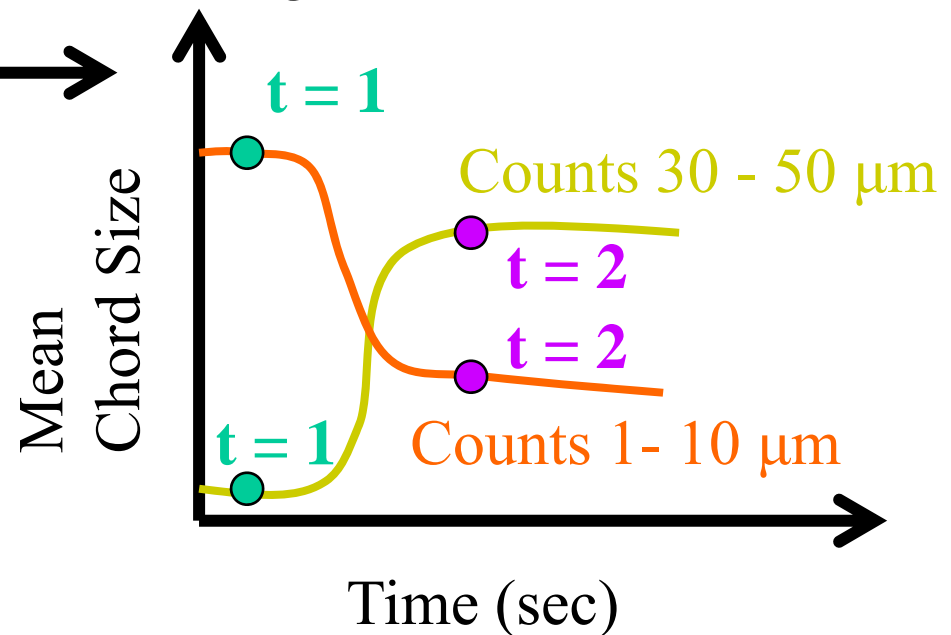
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Sample Data

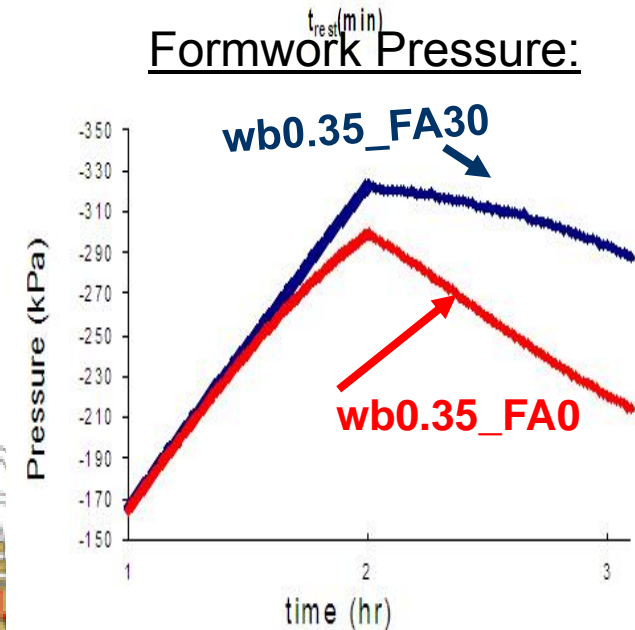
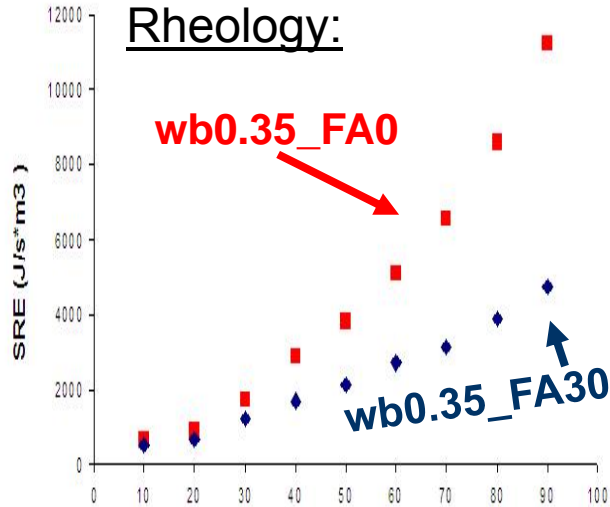


Statistics calculated from chord length distribution with time

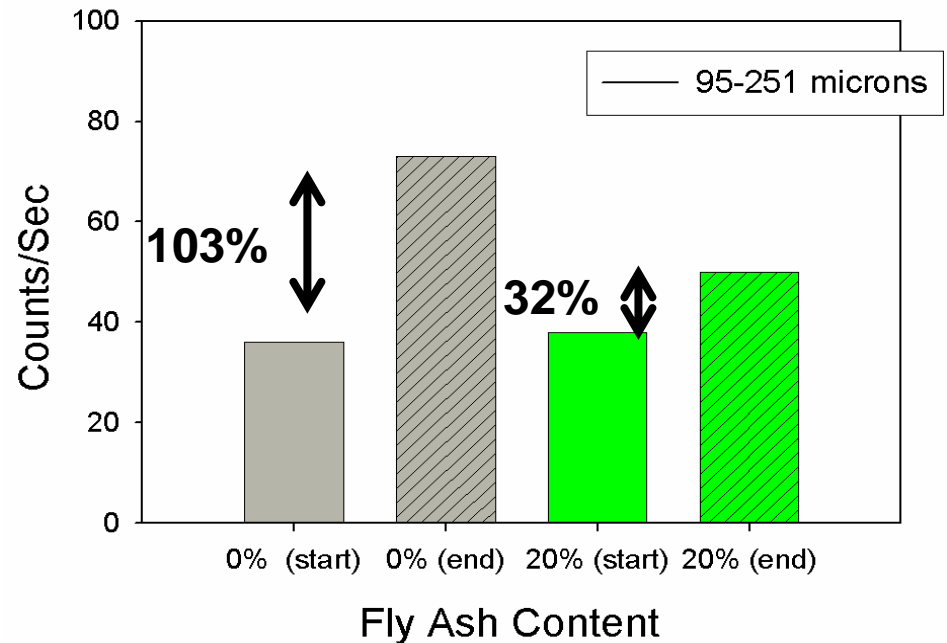




Linking Together Rheology, Formwork Pressure, and Flocculation



Number of counts at end of 30 minute buildup



Fly ash decreases flocculation



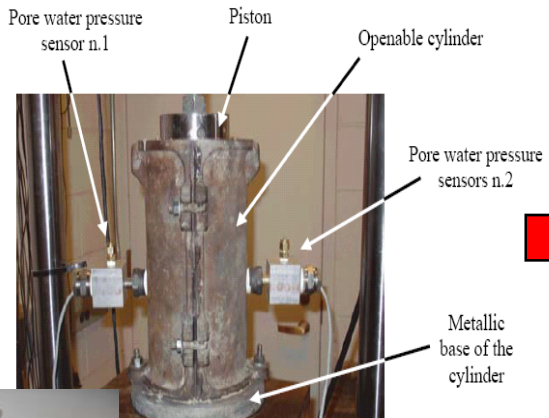
Linking Together



Floculation



Rheology



Pressure



Chemistry



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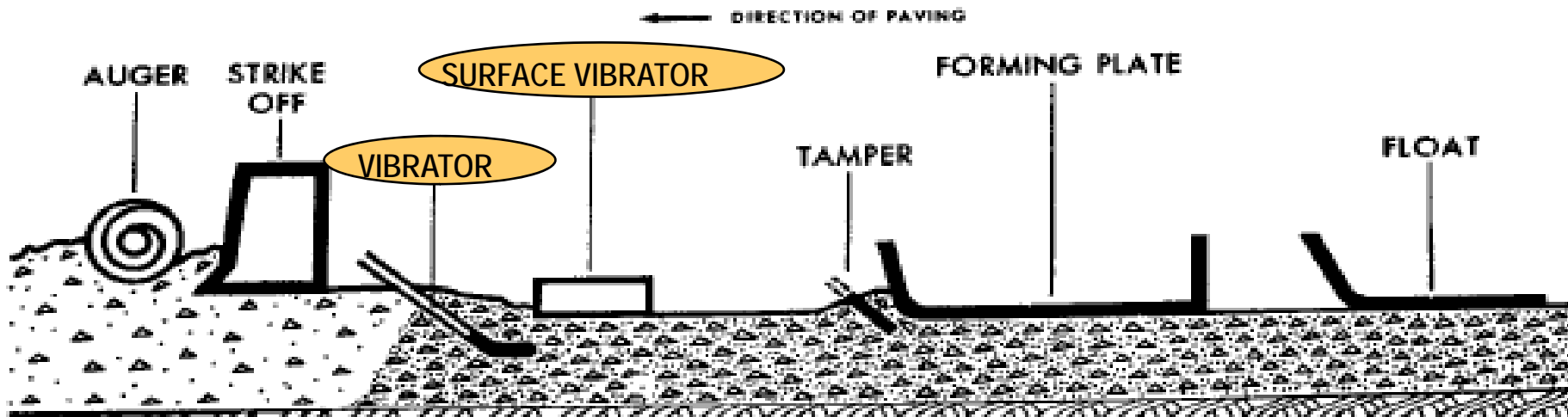


Applying SCC Technology to Slipform Pavements





Slipform Paving Process





Durability issues

- Slipform paving durability issues arise due to internal vibration (*loss of air content, segregation*)
- Eliminate need for internal vibration by manipulating the mix design...





Experimental Approach

- Modification of conventional SCC until shape stable



Conventional SCC

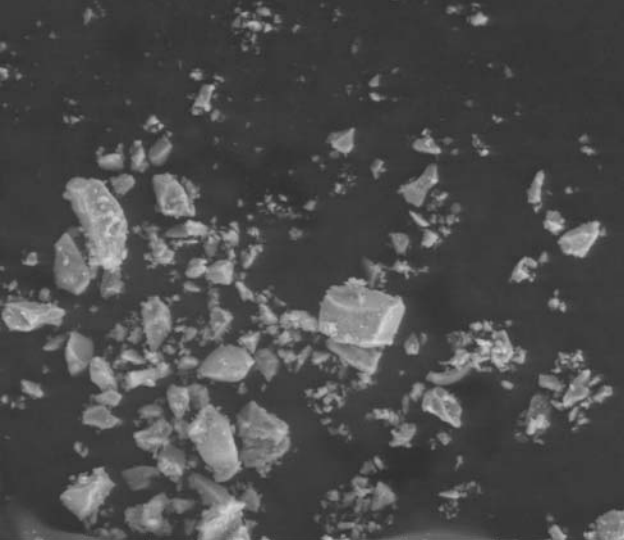


- Various Additives (clay, fly ash)
- Type and Amount of Plasticizer



Slipform SCC

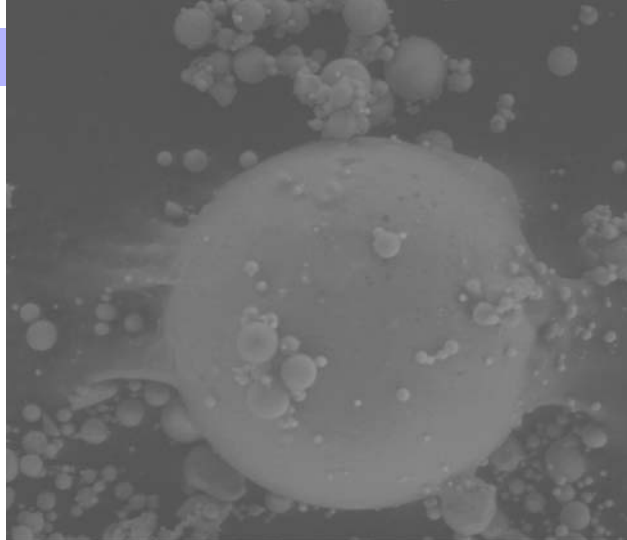
Ultimate Goal: Eliminate Internal Vibration



7/11/2005 WD Mag Spot Det Pressure HV VacMode
4:39:16 PM 9.0 mm 2176x 3.0 LFD 1.50 Torr 15.0 kV Low vacuum

Cement

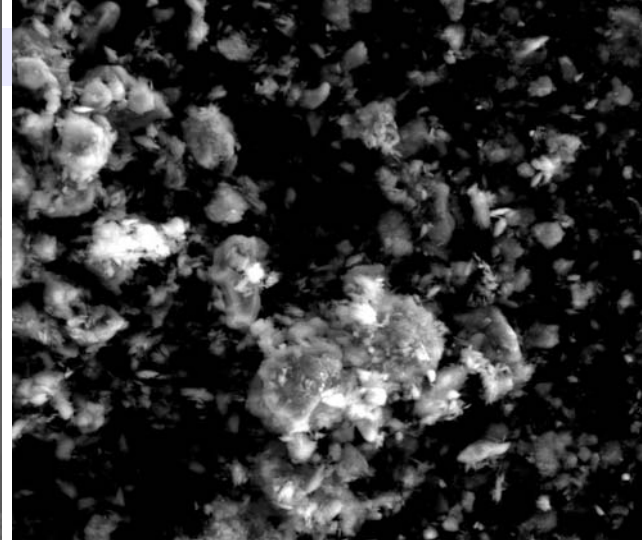
20 μ m



7/11/2005 WD Mag Spot Det Pressure HV VacMode
3:18:46 PM 8.8 mm 1655x 3.0 LFD 1.50 Torr 10.0 kV Low vacuum

Fly Ash

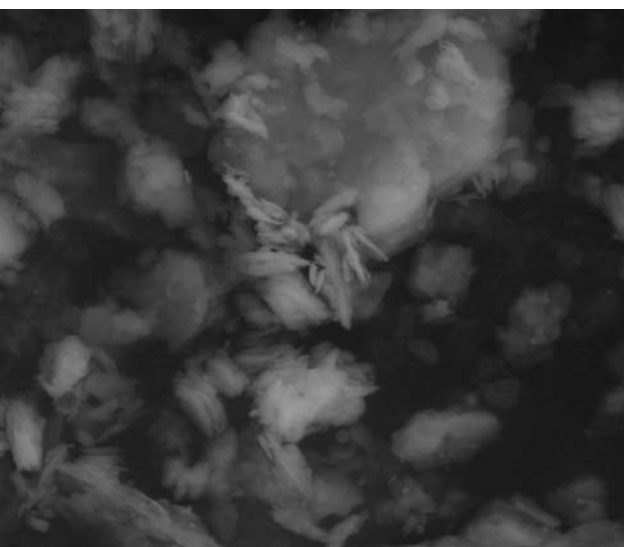
10 μ m



9/13/2005 WD Mag Spot Det Pressure HV VacMode
12:00:37 PM 7.4 mm 2131x 3.0 LFD 0.75 Torr 20.0 kV Low vacuum

Concretosol

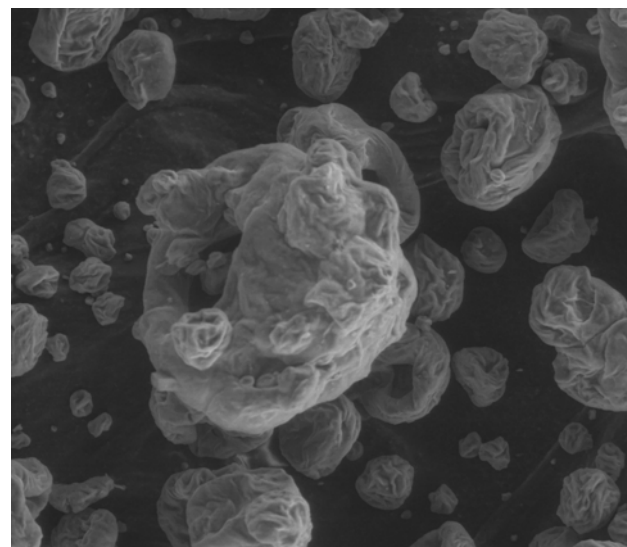
20 μ m



7/11/2005 WD Mag Spot Det Pressure HV VacMode
4:21:20 PM 9.0 mm 18998x 3.0 LFD 1.50 Torr 15.0 kV Low vacuum

Metamax

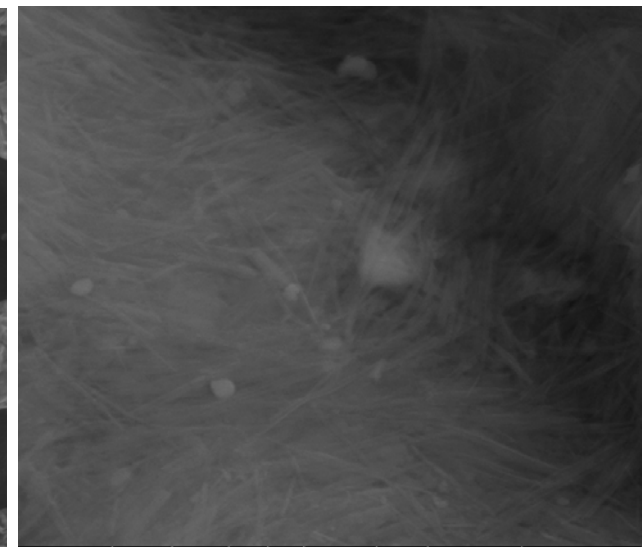
2 μ m



7/29/2005 WD Mag Spot Det Pressure HV VacMode
11:51:39 AM 8.0 mm 1045x 3.0 LFD 0.70 Torr 9.5 kV Low vacuum

Acti-Gel

50 μ m



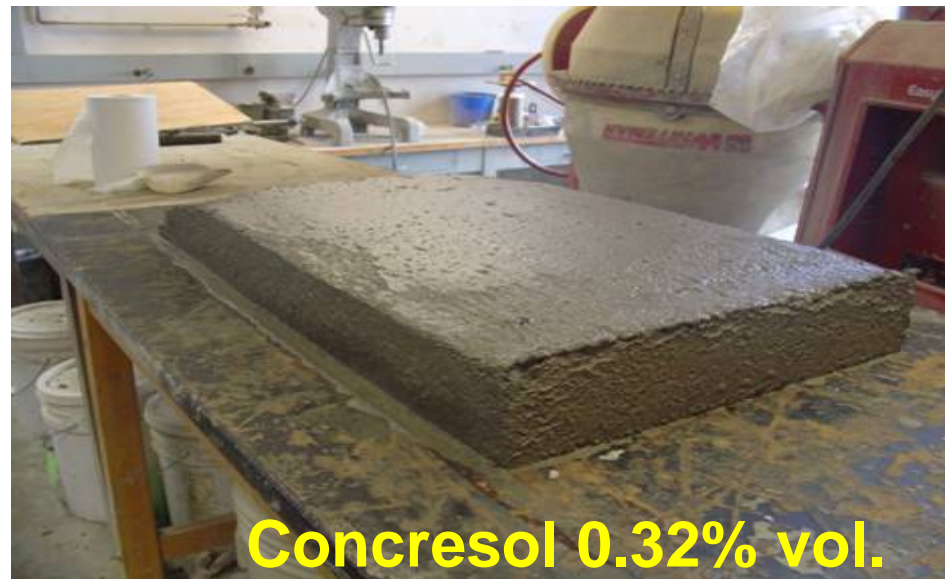
7/29/2005 WD Mag Spot Det Pressure HV VacMode
12:00:11 PM 7.9 mm 77835x 3.0 LFD 0.50 Torr 9.5 kV Low vacuum

Acti-Gel

500 nm



Effect of Materials on Shape and Surface





How Does Clay Affect Flocculation?

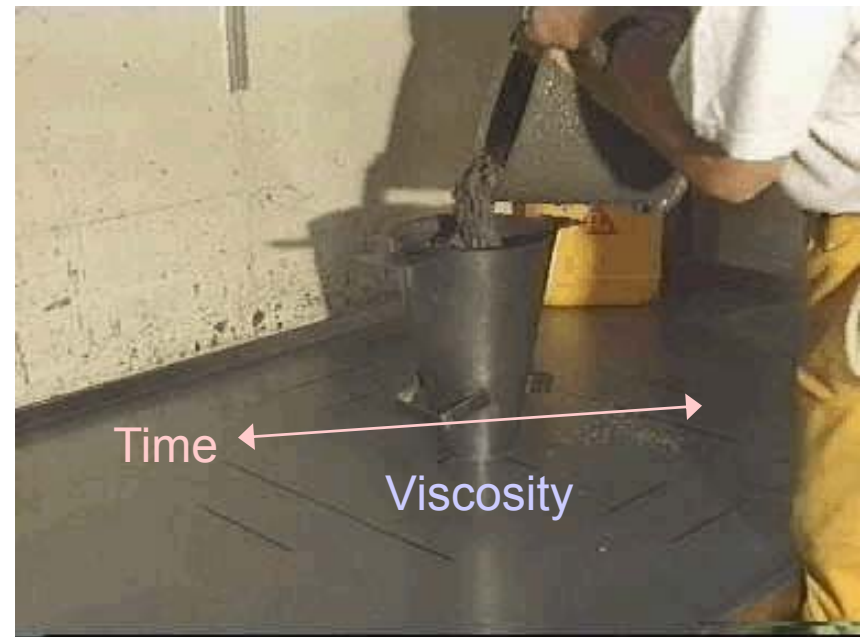
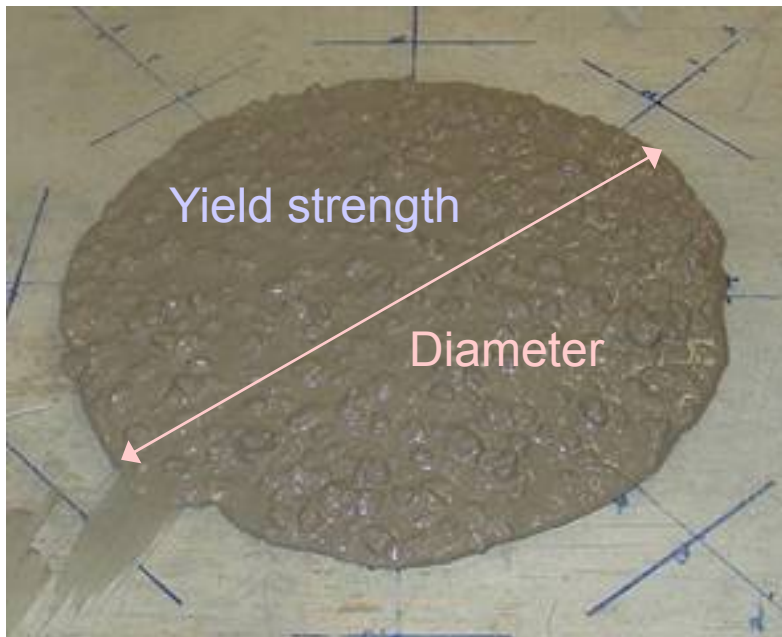
- Methods of investigation:
 - Shear rheology
 - Compressive rheology
 - Floc size determination





From Lab to Practice

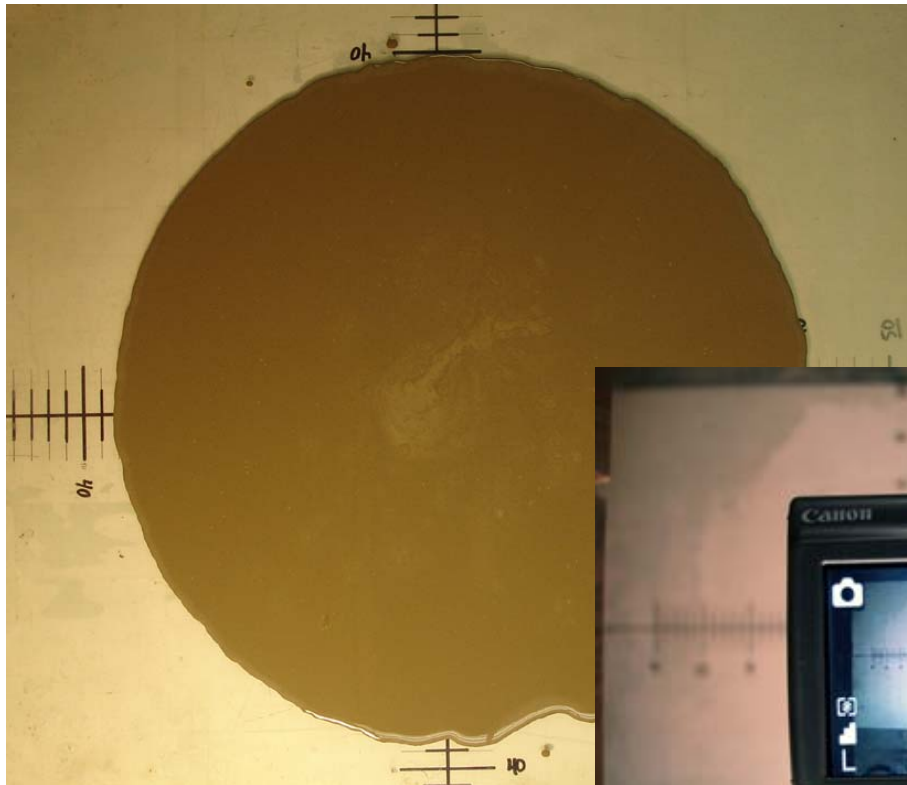
- Relating fundamental properties to common slump or flow tests
 - Final spread \Rightarrow yield strength?
 - Time to final spread \Rightarrow viscosity?





Experimental Setup

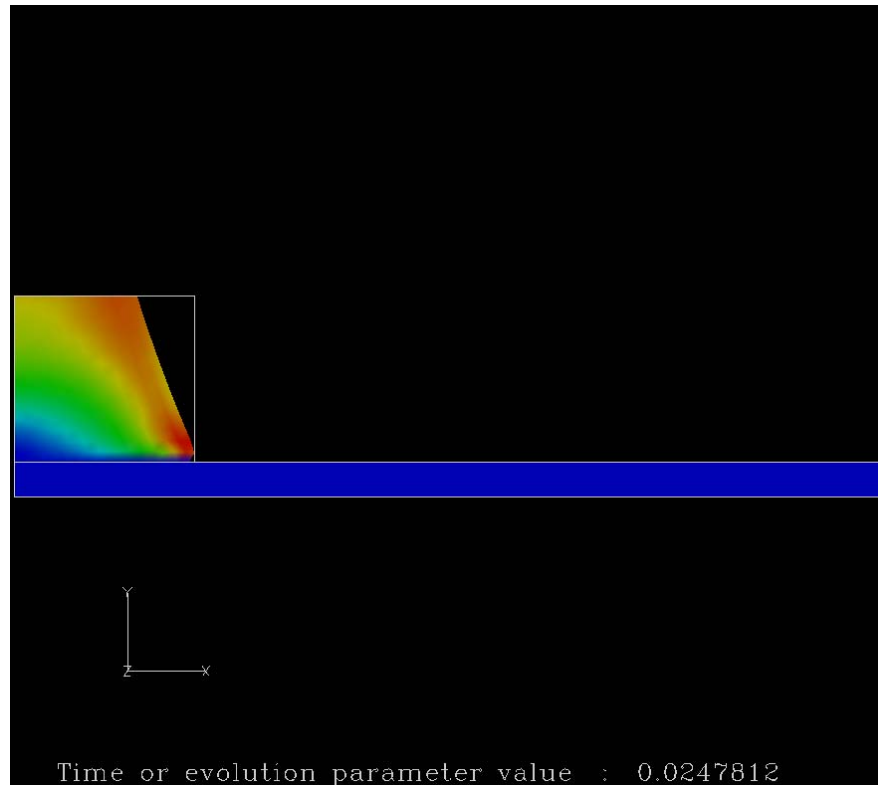
- Measuring final diameter and time it takes to reach a given diameter for cement paste





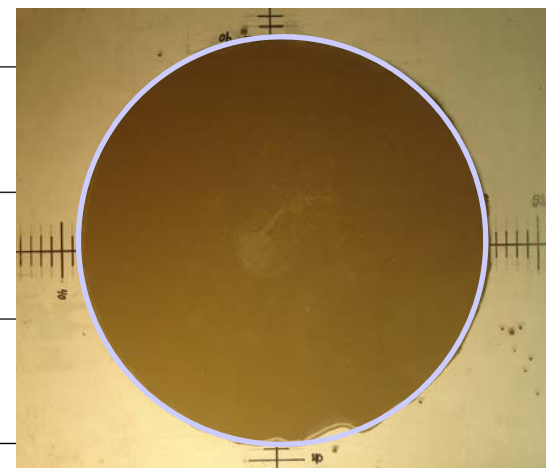
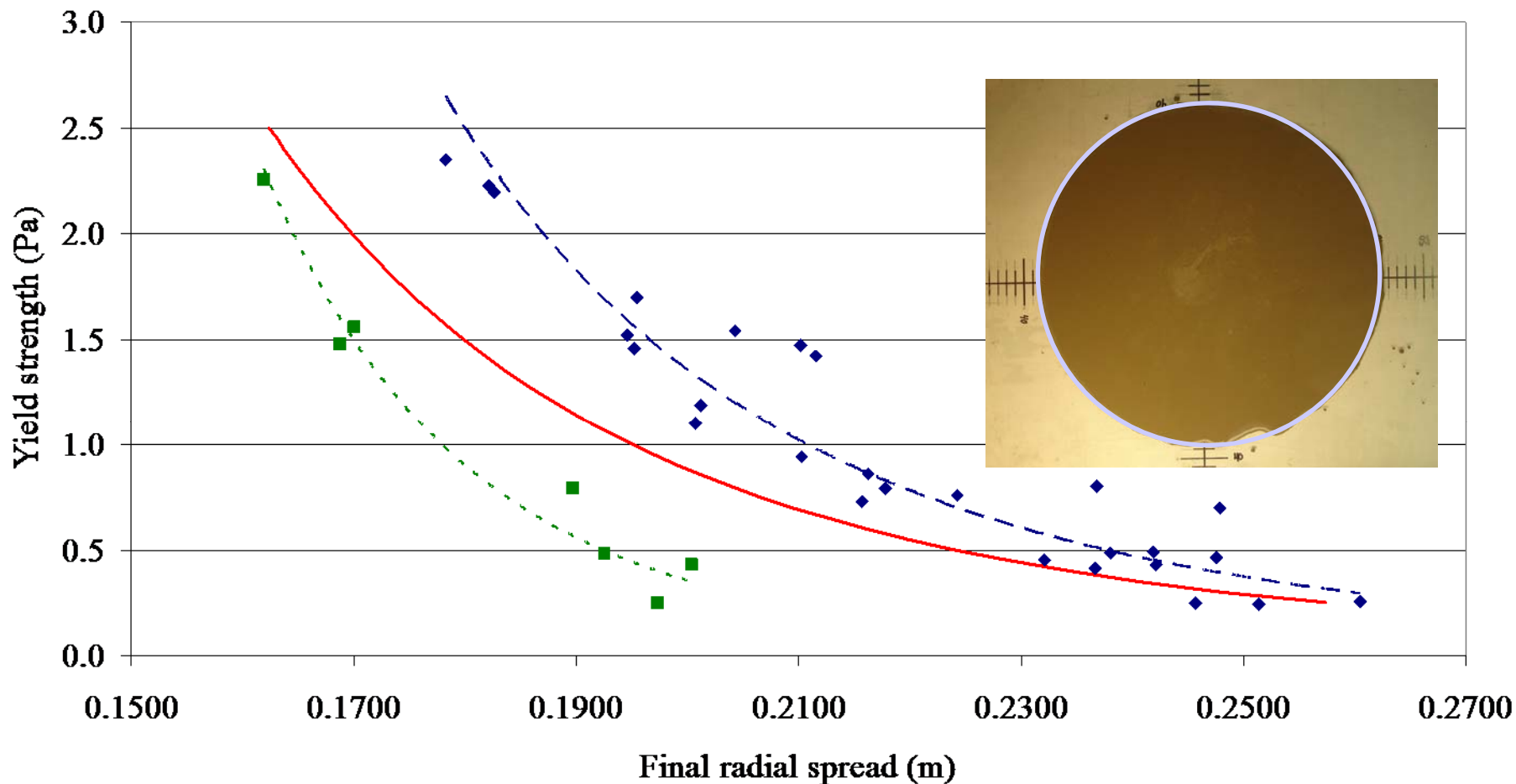
Modeling Setup

- Using Fluent's POLYFLOW to numerically simulate the flow of cement paste





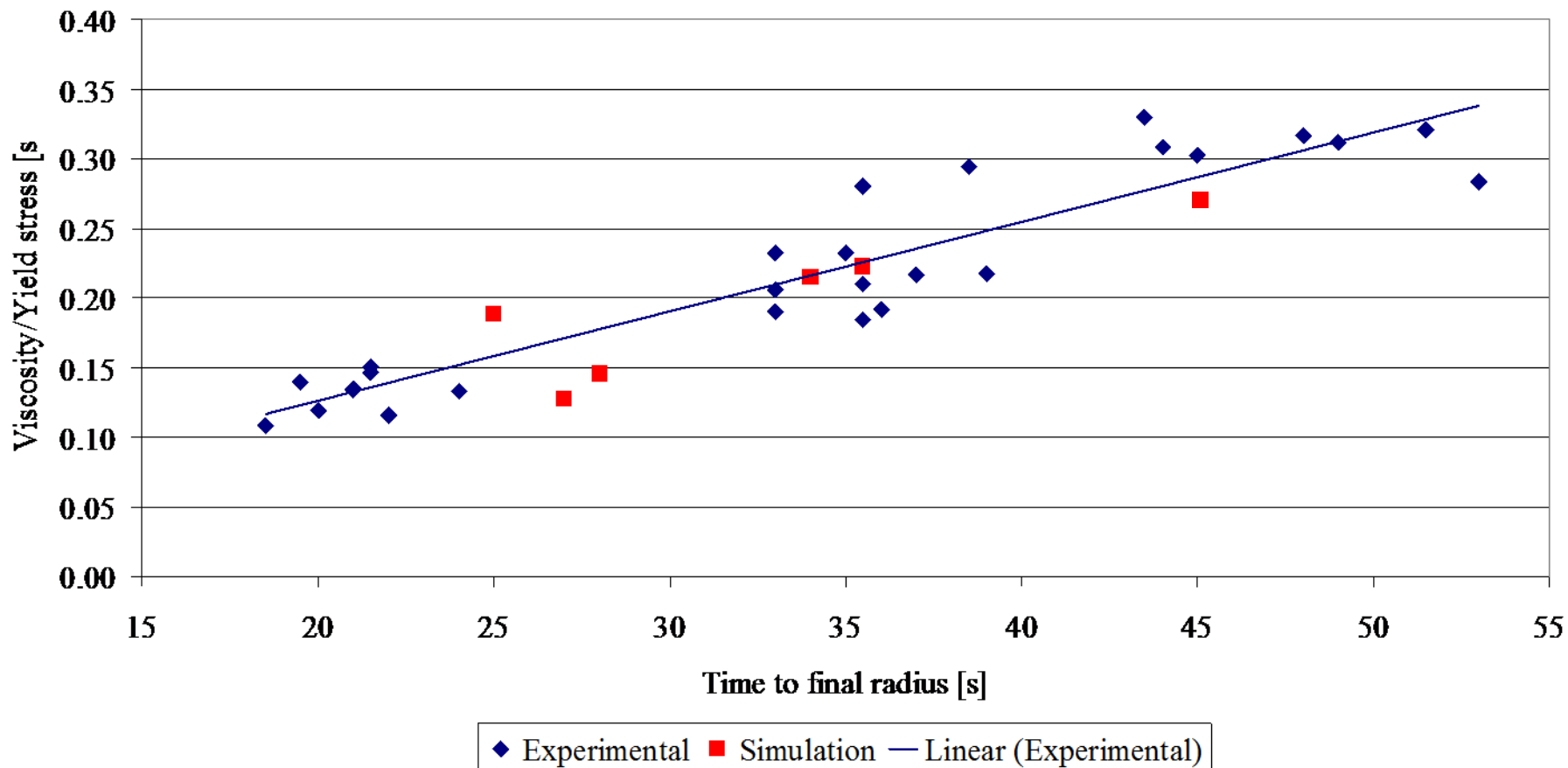
Yield Strength – Final Spread Relationship



◆ Experiment — Theory w/o surface tension ■ Simulation - - Power (Experiment) ··· Power (Simulation)



Viscosity / Yield Stress – Final Time Relationship

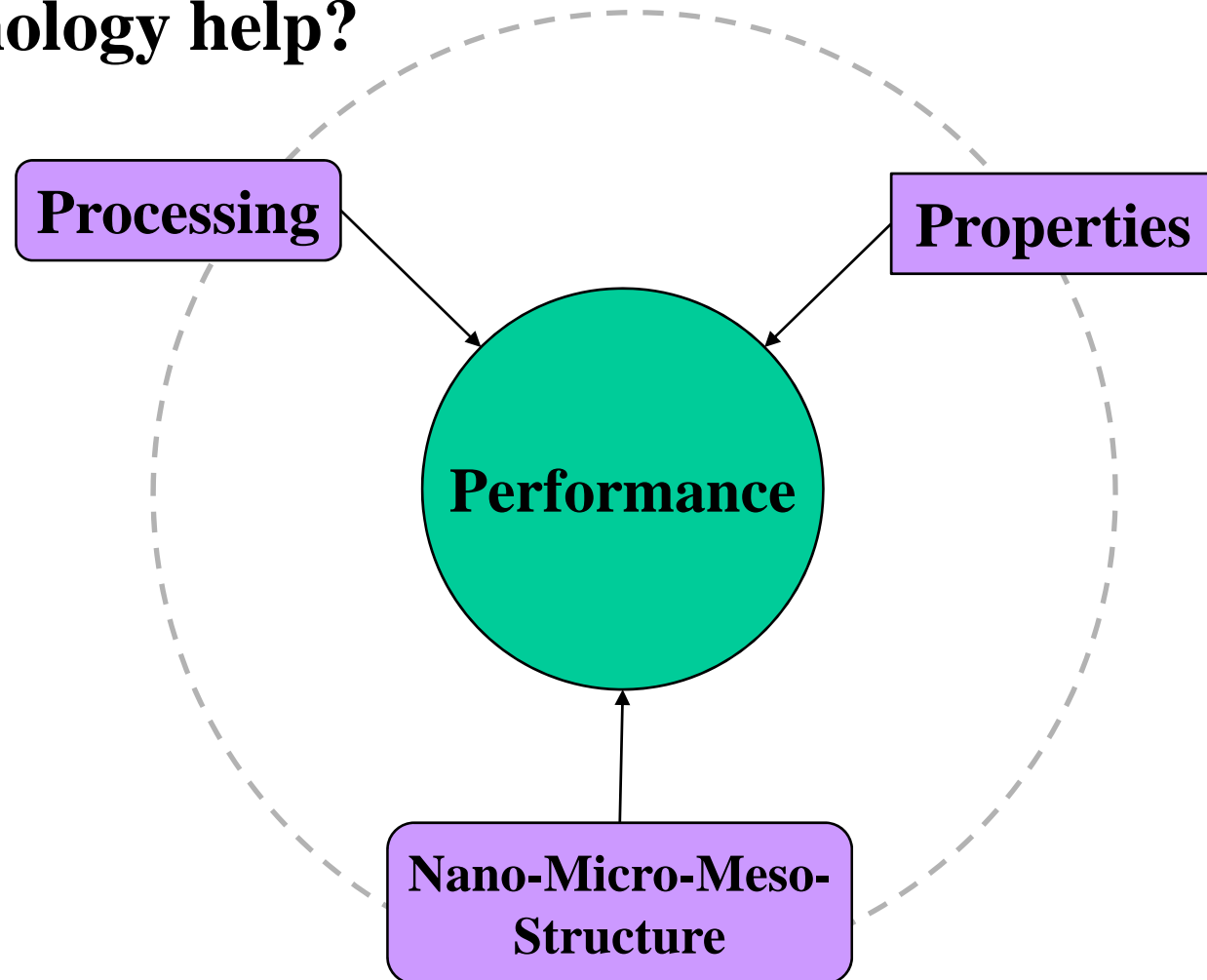




Nanomodification of Cementitious Materials

How can Nanotechnology help?

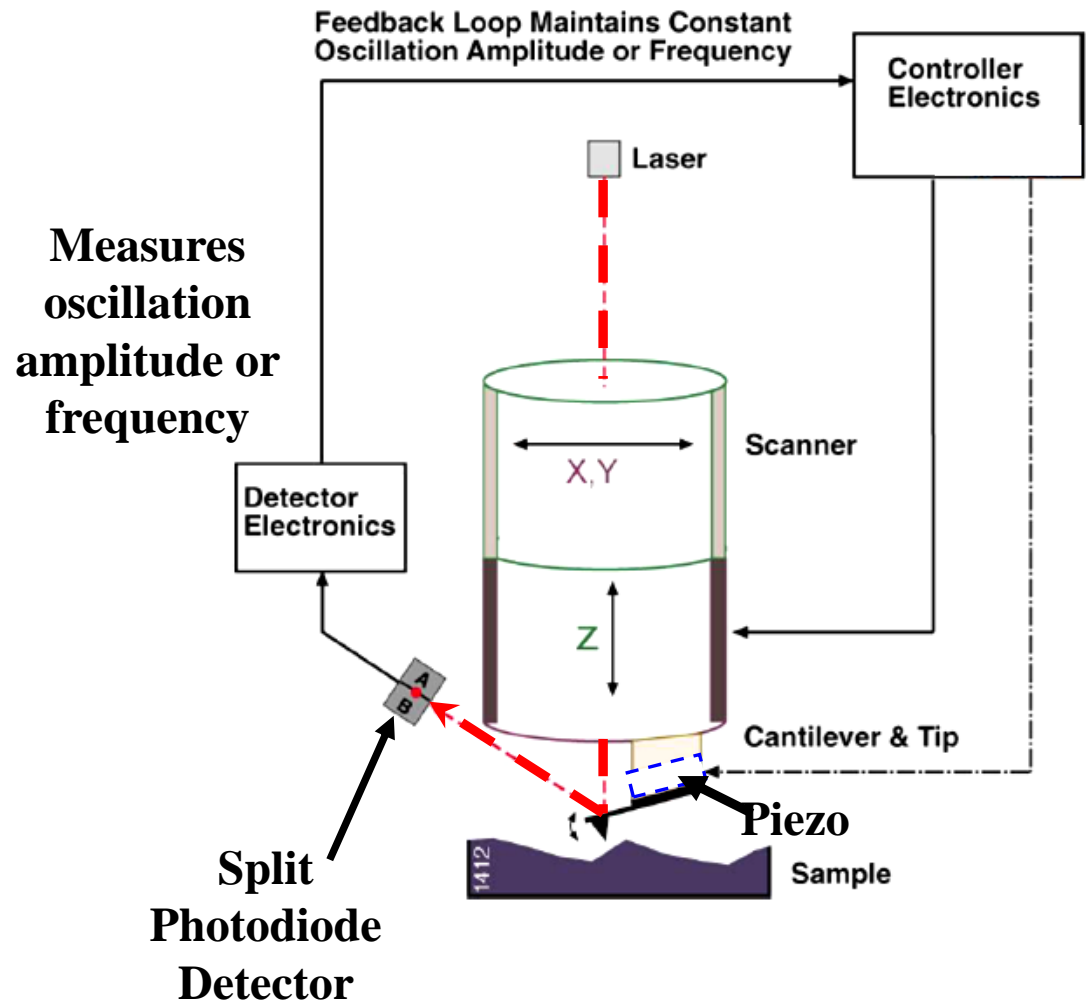
- **Characterization**
- **New materials**
- **Sensors**





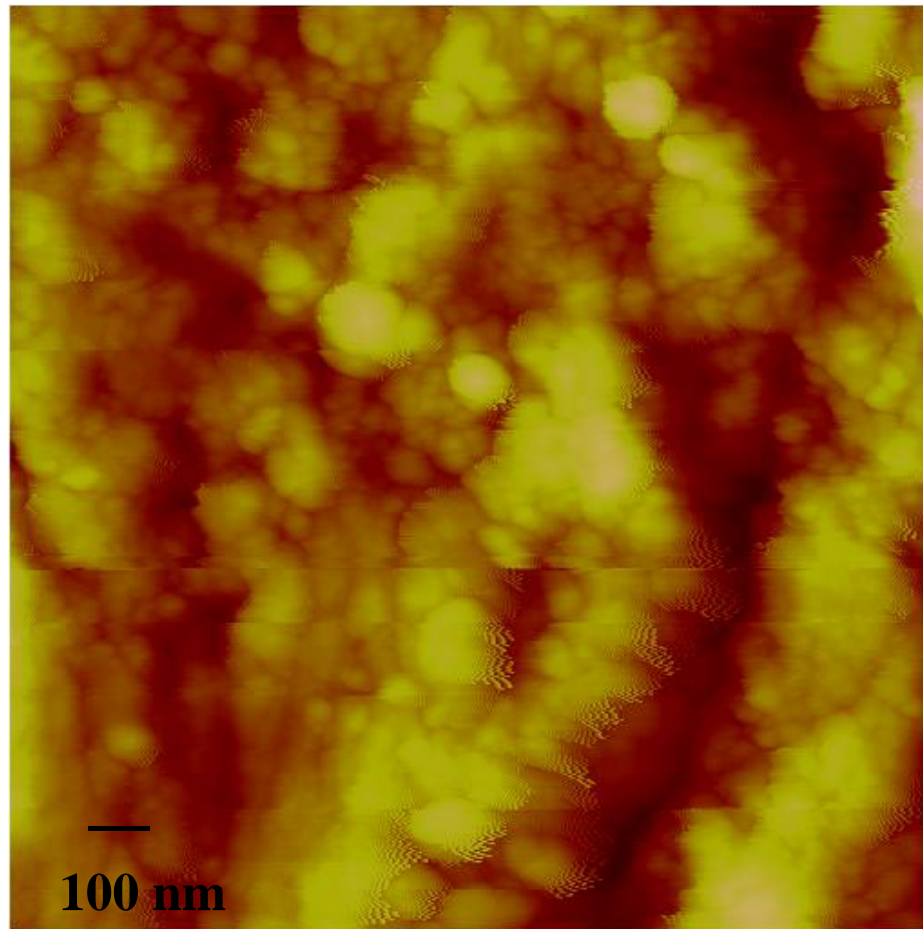
Atomic Force Microscopy

- Images sample surface at nano-scale
- Abilities:
 - Normal atmospheric temperature and pressure
 - Under liquid
 - Determines mechanical properties (Young's modulus) in conjunction with imaging





Atomic Force Microscopy Image of Calcium Silicate Hydrate (C-S-H)

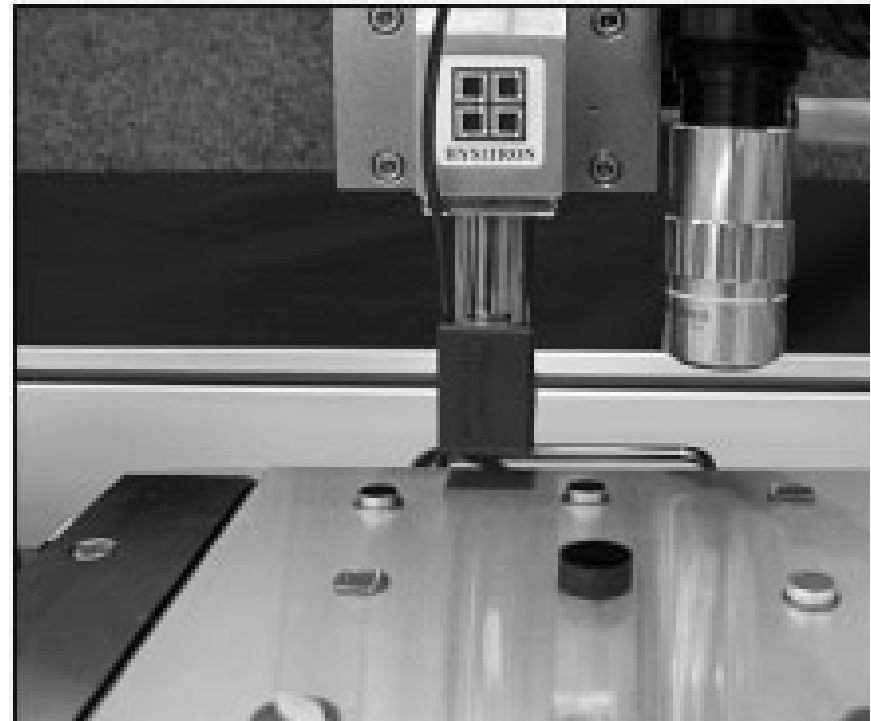
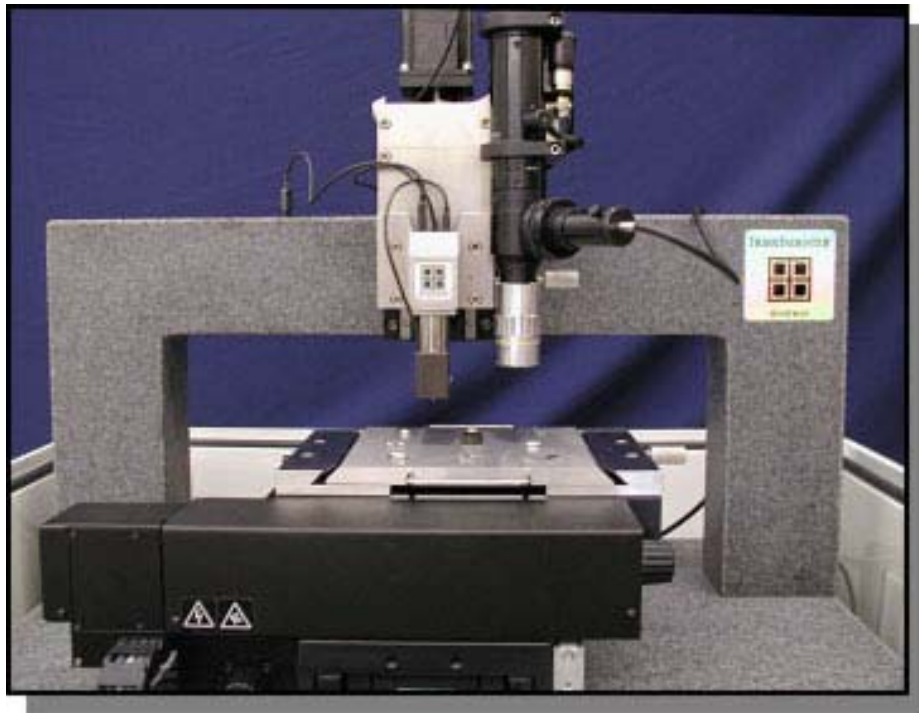


- Image size: $1.5 \mu\text{m} \times 1.5 \mu\text{m}$, spherical particles of the order of 40 nm
- Maximum height difference between different points $\sim 0.3 \mu\text{m}$



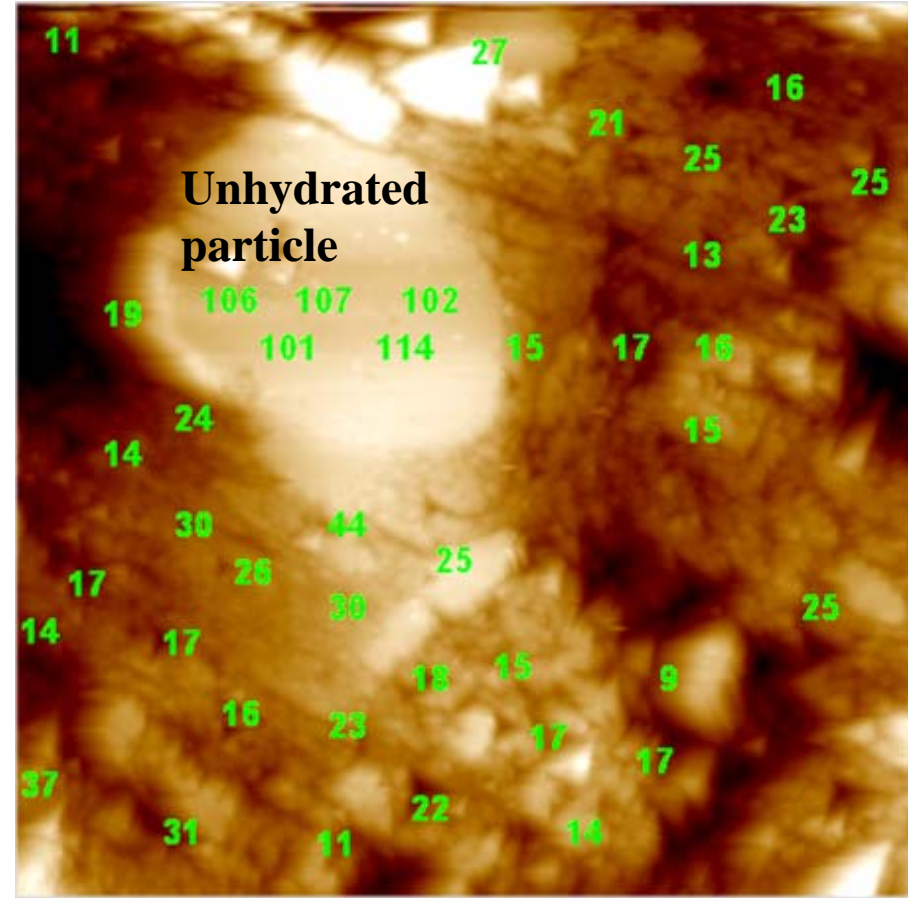
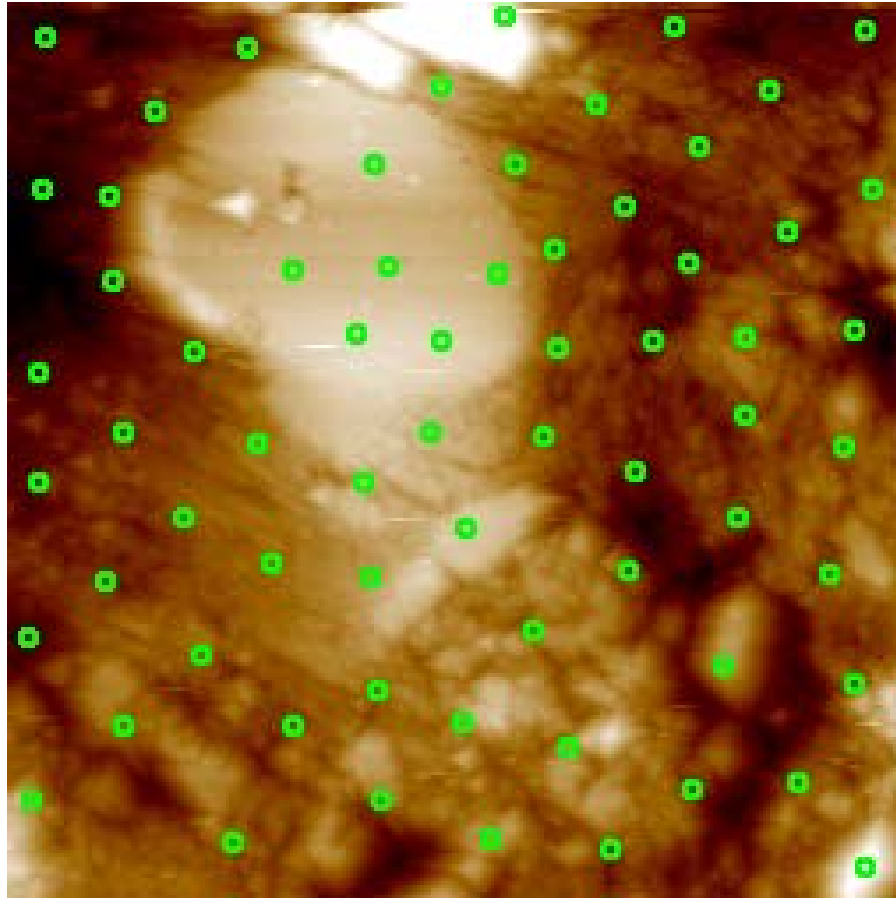
Hysitron Triboindenter

- Can do both nanoindentation and scanning probe microscopy imaging
- Berkovich tip has been used





Nanoindentation on 6 Months Old Cement Paste: w/c 0.5

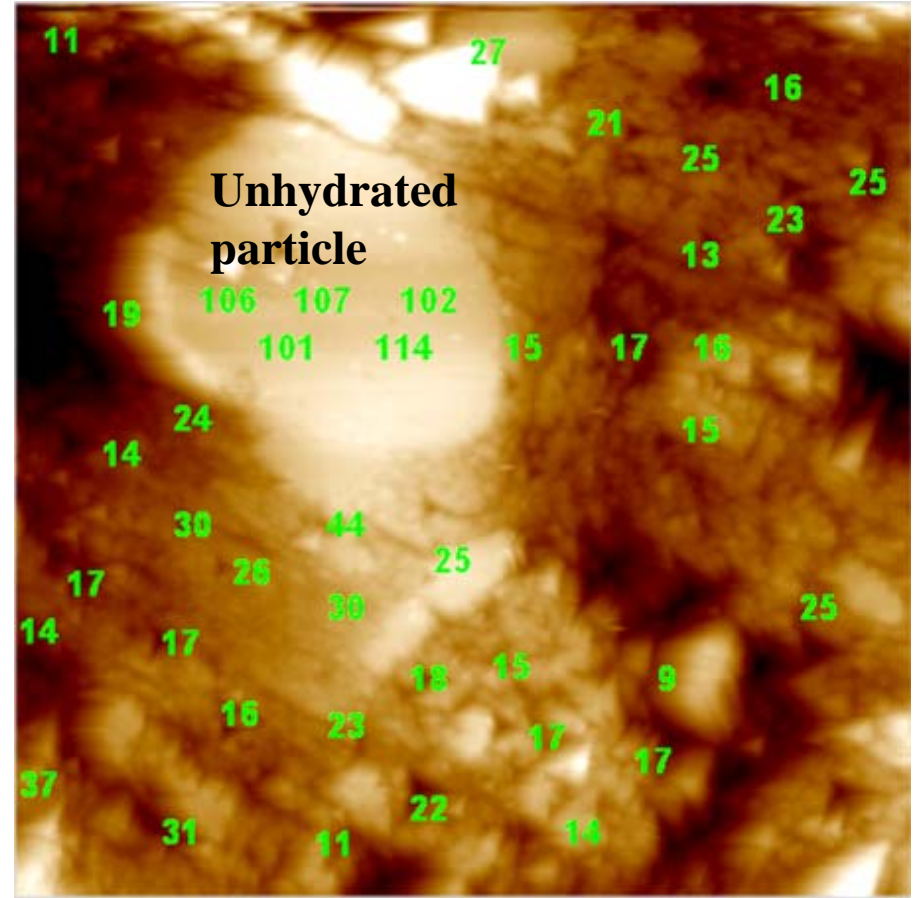


Unhydrated
particle

- Image size: 60 μm x 60 μm
- Left image shows indent locations, right image shows Young's Modulus in GPa



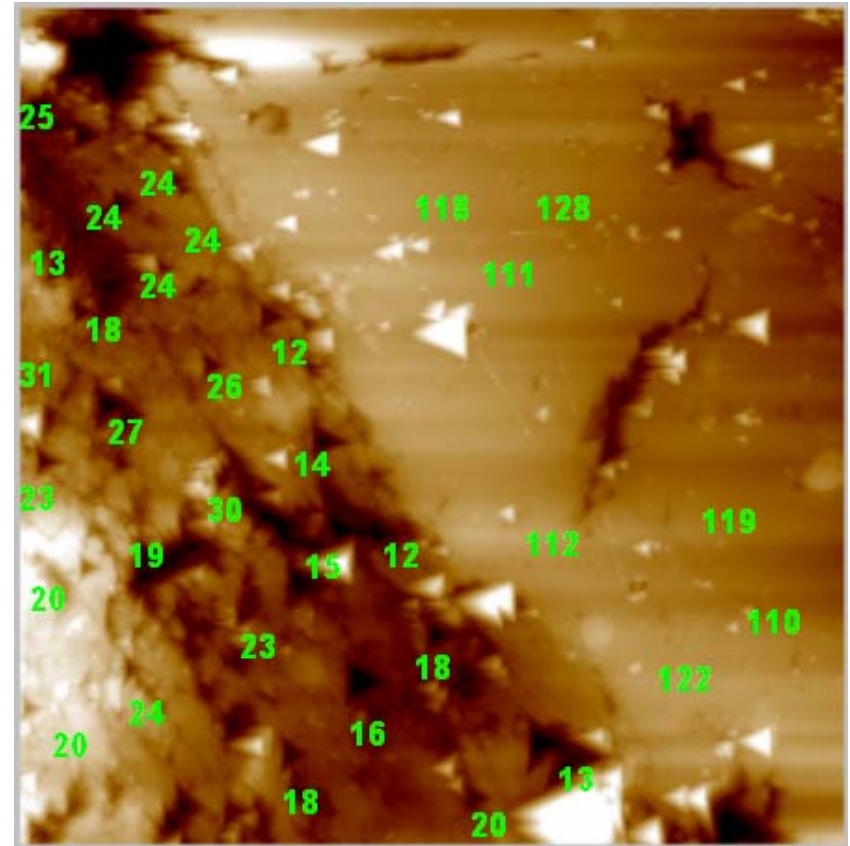
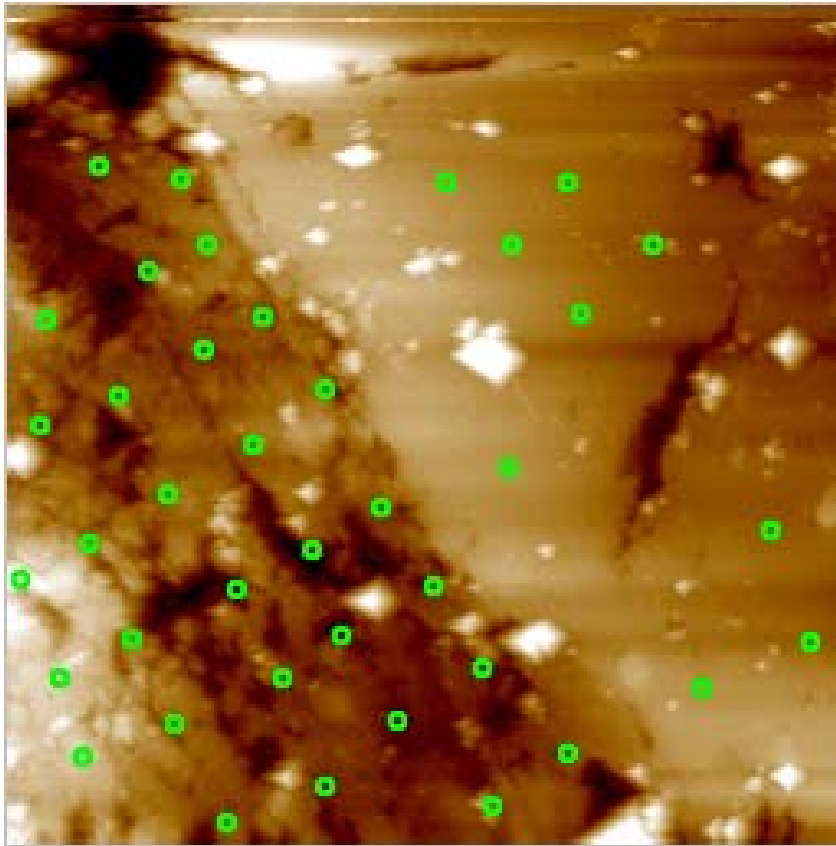
Nanoindentation on 6 Months Old Cement Paste: w/c 0.5



- Image size: 60 μm x 60 μm
- Left image shows indent locations, right image shows Young's Modulus in GPa



Nanoindentation on Sand, ITZ and Paste Matrix



- Image size: 60 μm x 60 μm
- Left image shows indent locations, right image shows Young's Modulus in GPa



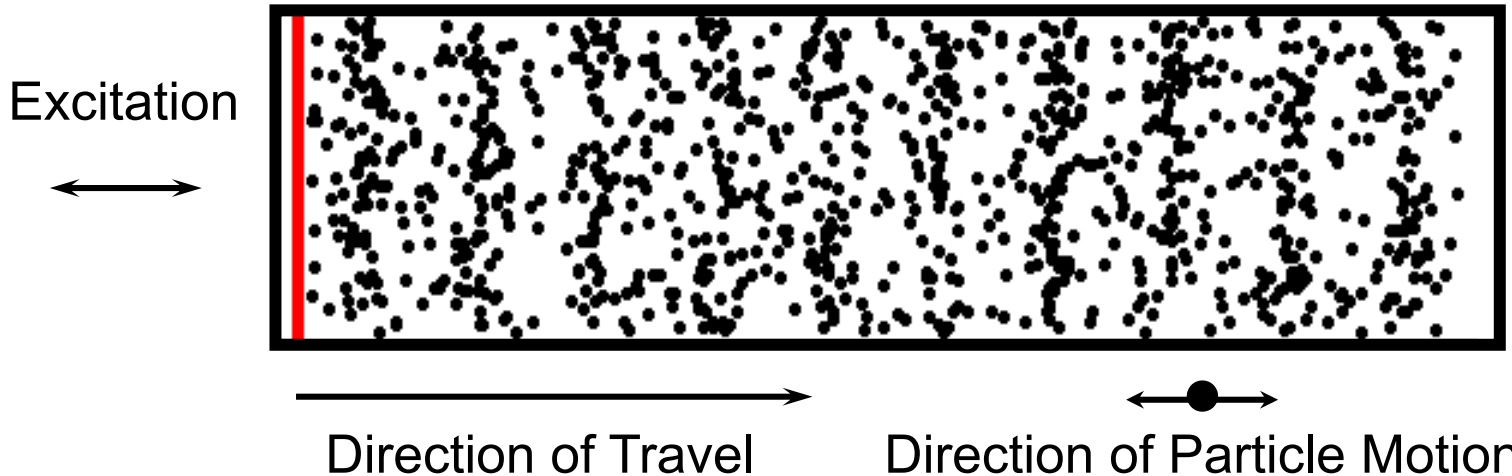
Sensors

- Impedance Spectroscopy
- Ultrasonic Sensing System
- Nuclear Magnetic Resonance
- Dielectric Measurements with Microwaves



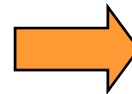
Ultrasonic Sensing: Early Age Monitoring with Wave Reflection

Longitudinal waves (L-waves)
[also: Primary (P-) Waves, Compression Waves]



Wave Velocity:

$$v_L = \sqrt{\frac{E(1-\nu)}{\rho(1+\nu)(1-2\nu)}}$$



Governing Parameters

Young's Modulus E

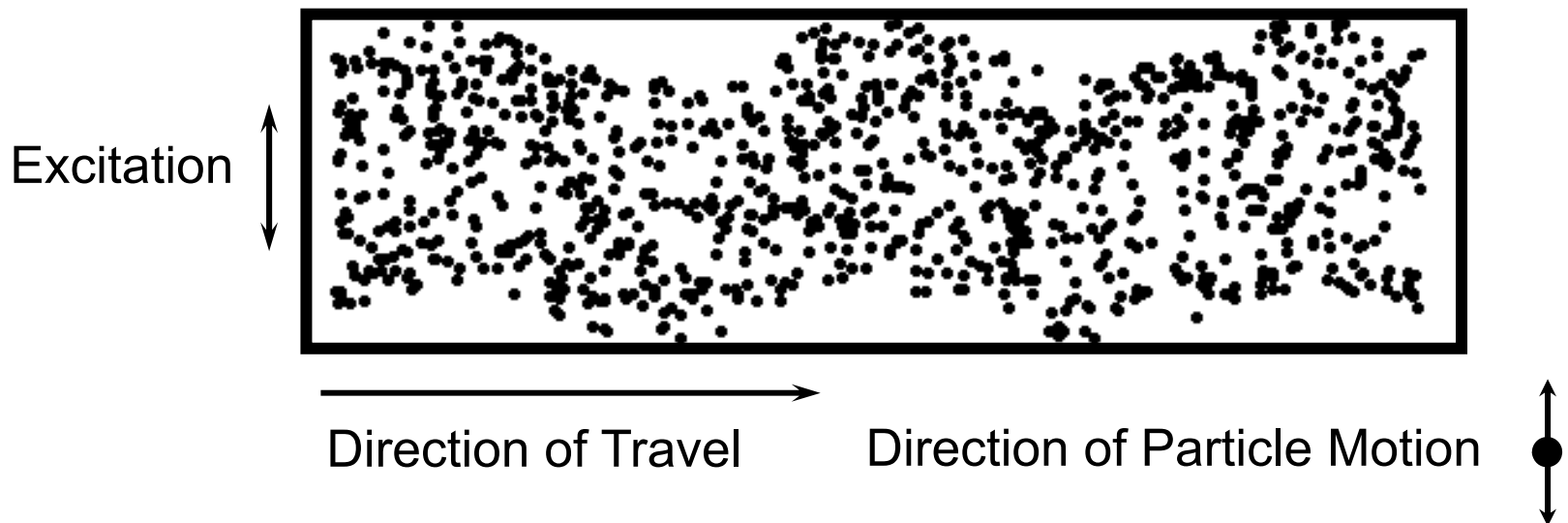
Poisson's Ratio ν

Density ρ



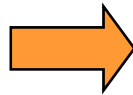
Transverse Waves (T-waves)

also: Secondary (S-) Waves, Shear Waves



Wave Velocity:

$$v_T = \sqrt{\frac{G}{\rho}}$$



Governing Parameters

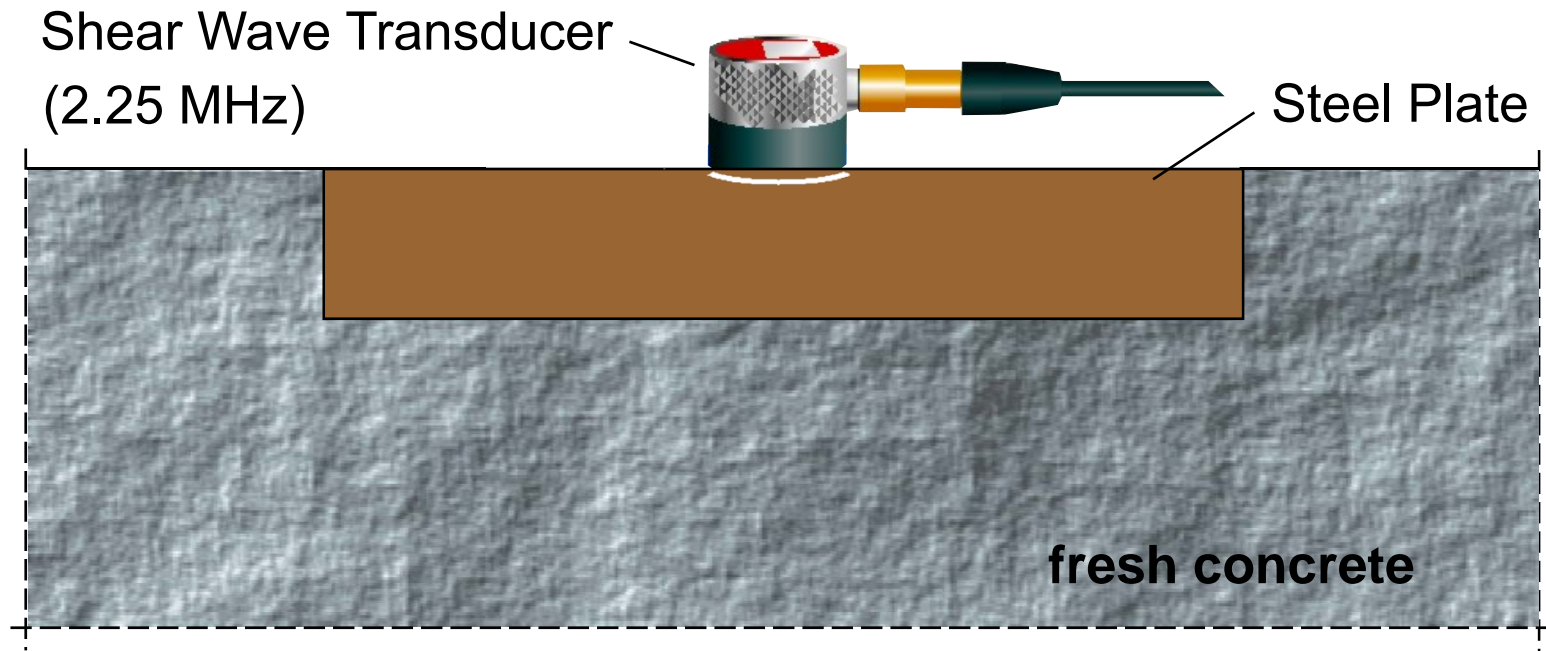
Shear Modulus G

Density ρ

no propagation in liquids or gases !



Principle of Wave Reflection Method



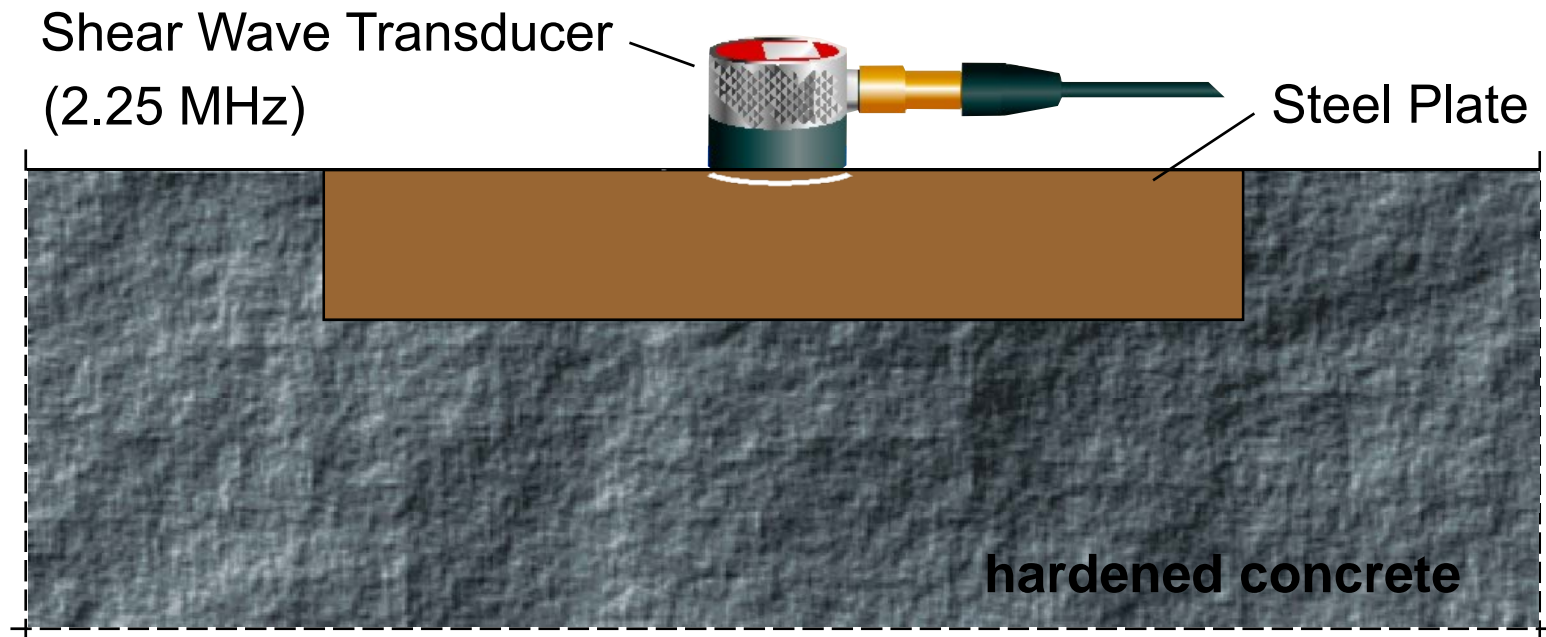
Case 1: concrete is liquid

No wave transmission at interface

Shear waves: do not propagate in liquids



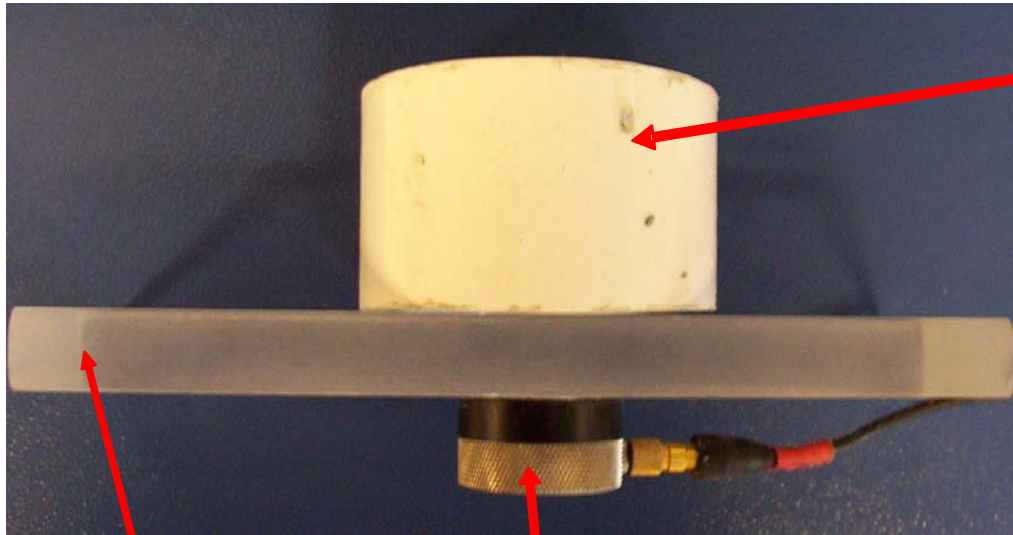
Principle of Wave Reflection Method



Case 2: concrete is hardening
Transmission losses at interface



Ultrasonic Sensing: Experimental Setup



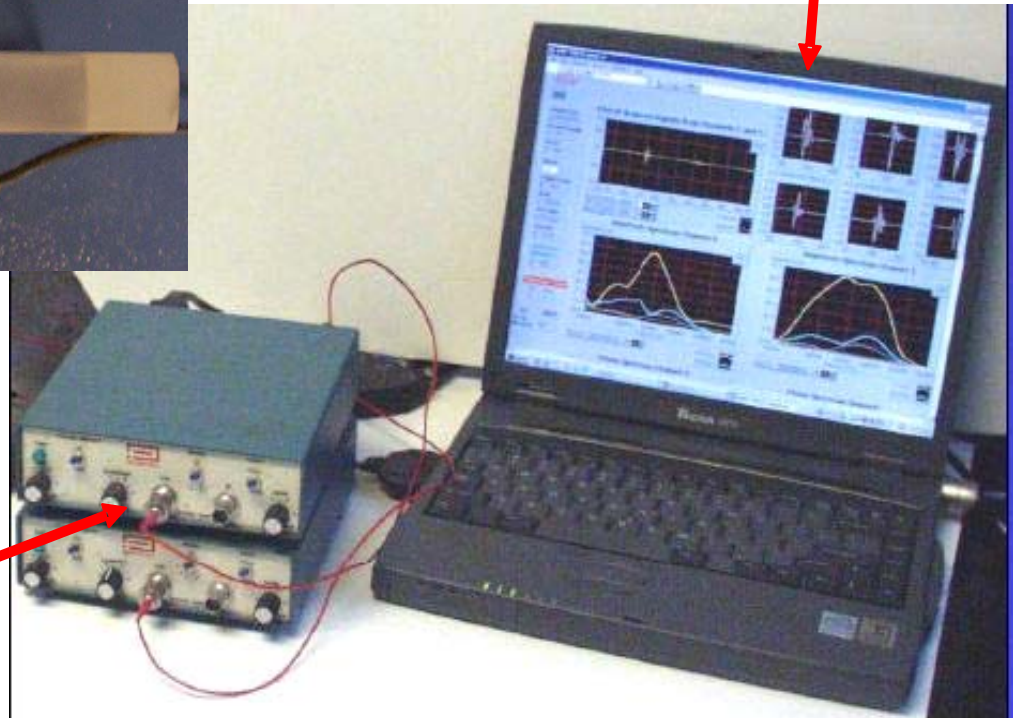
Fresh
cement paste

Computer

Buffer material Transducer (2.25MHz)

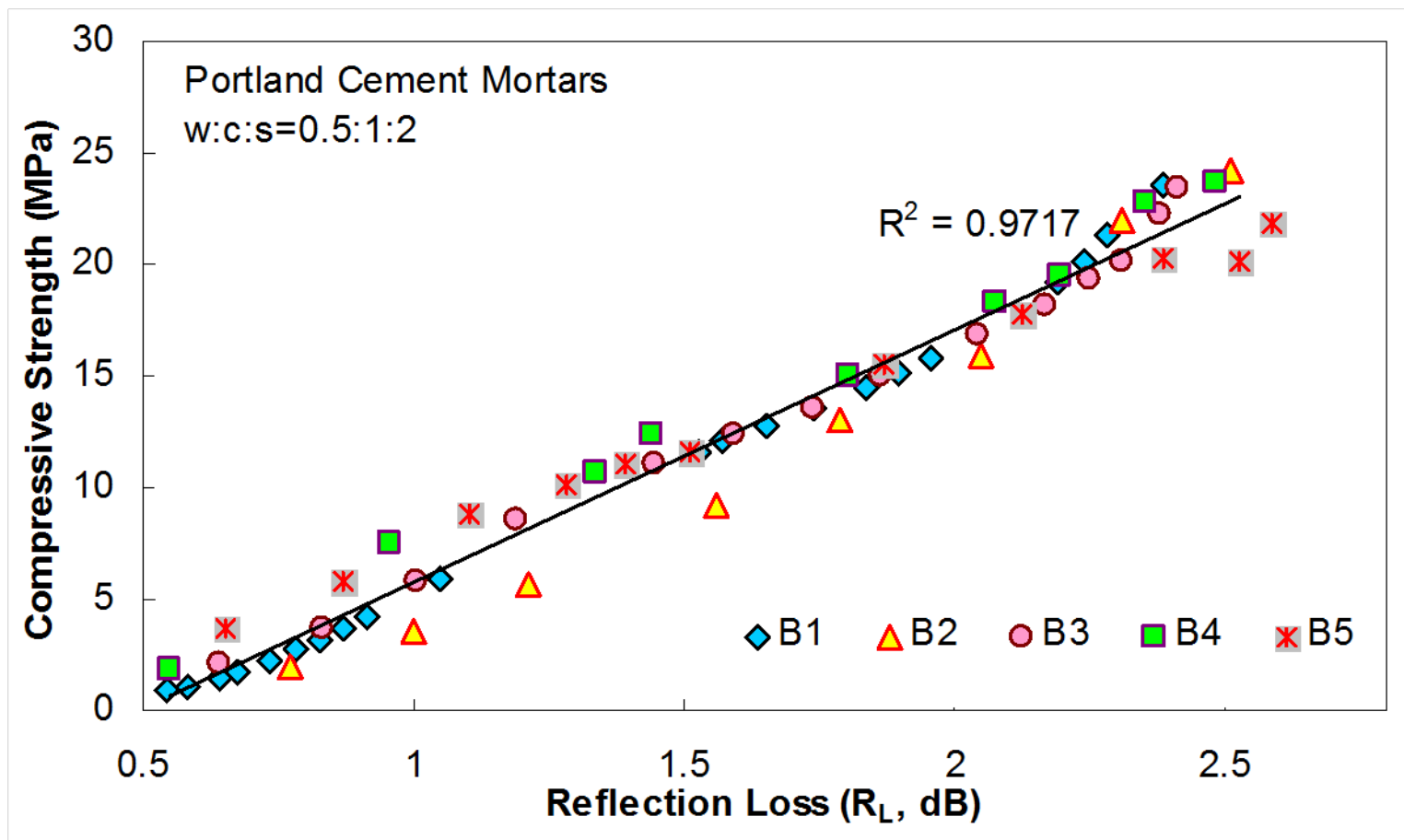
Wavelength: $\sim 0.1-1\mu\text{m}$
at early ages

Pulser



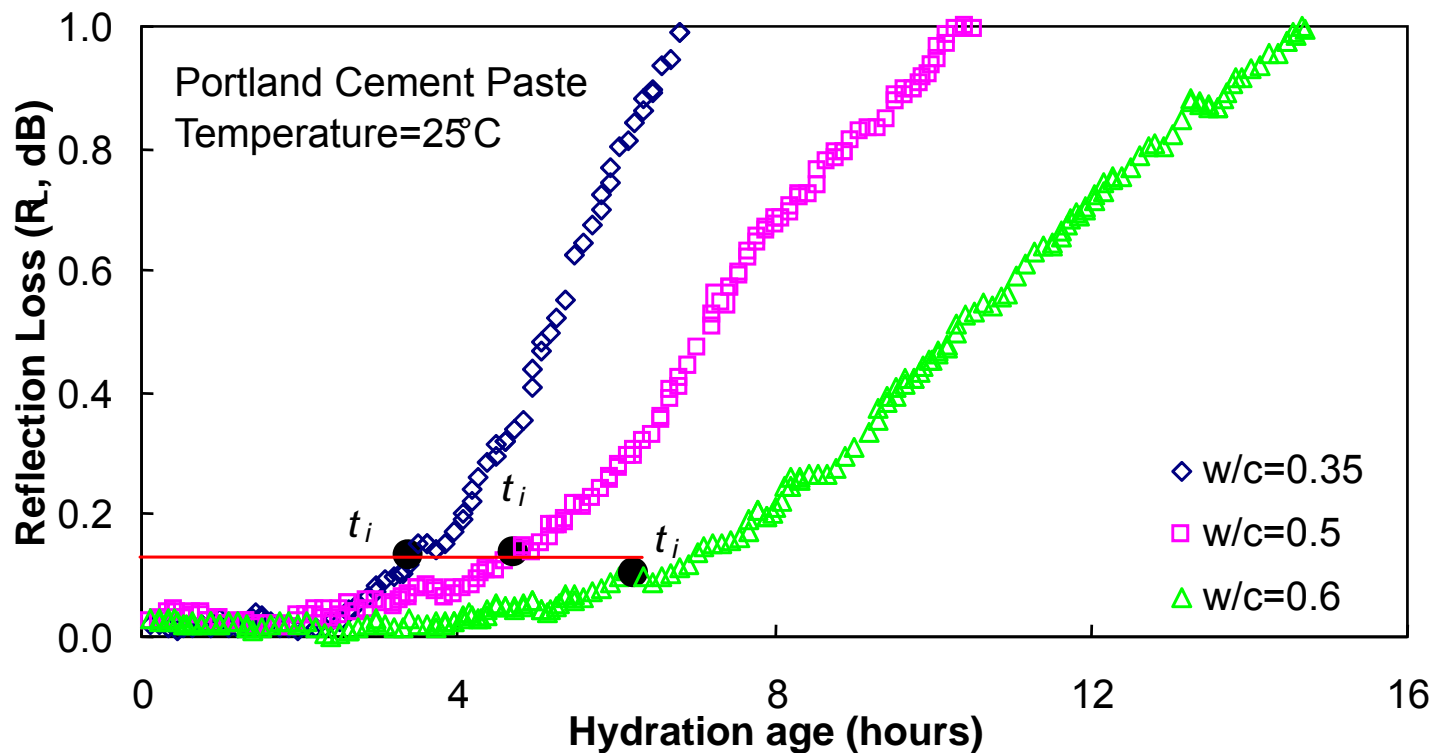


Compressive Strength Correlation with Reflection Loss





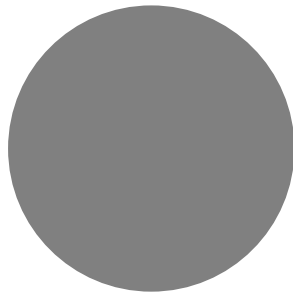
Reflection Loss and Initial Setting Time



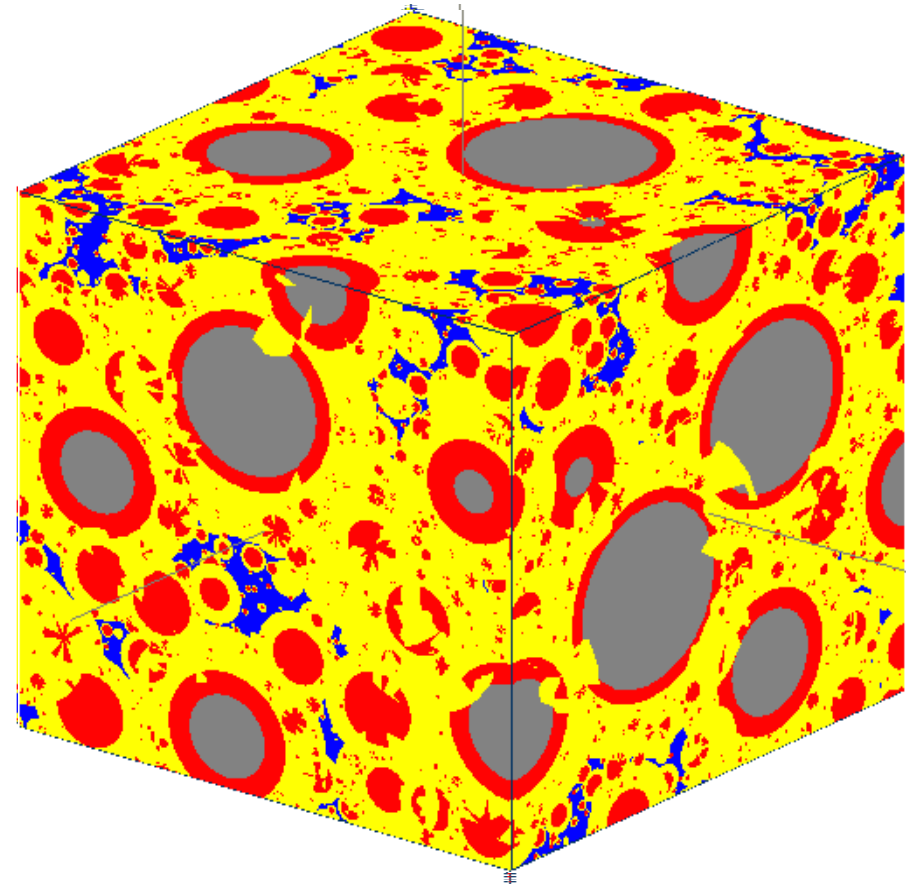
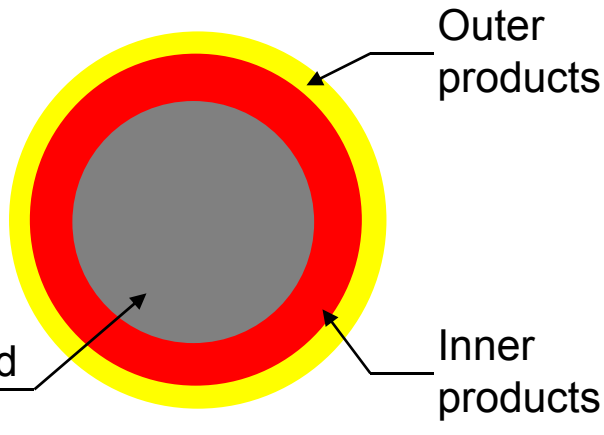


How Can R_L be Related to Microstructural Changes?

Initial stage

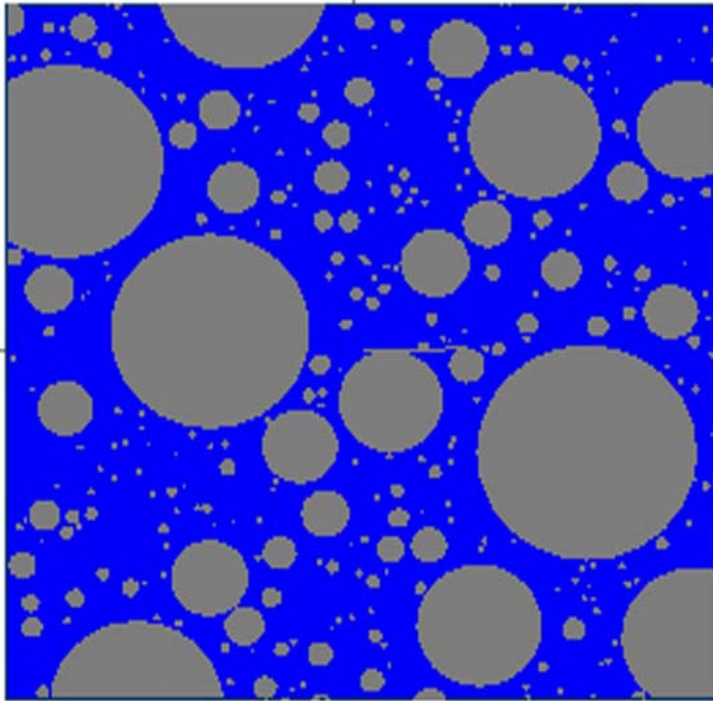


During hydration

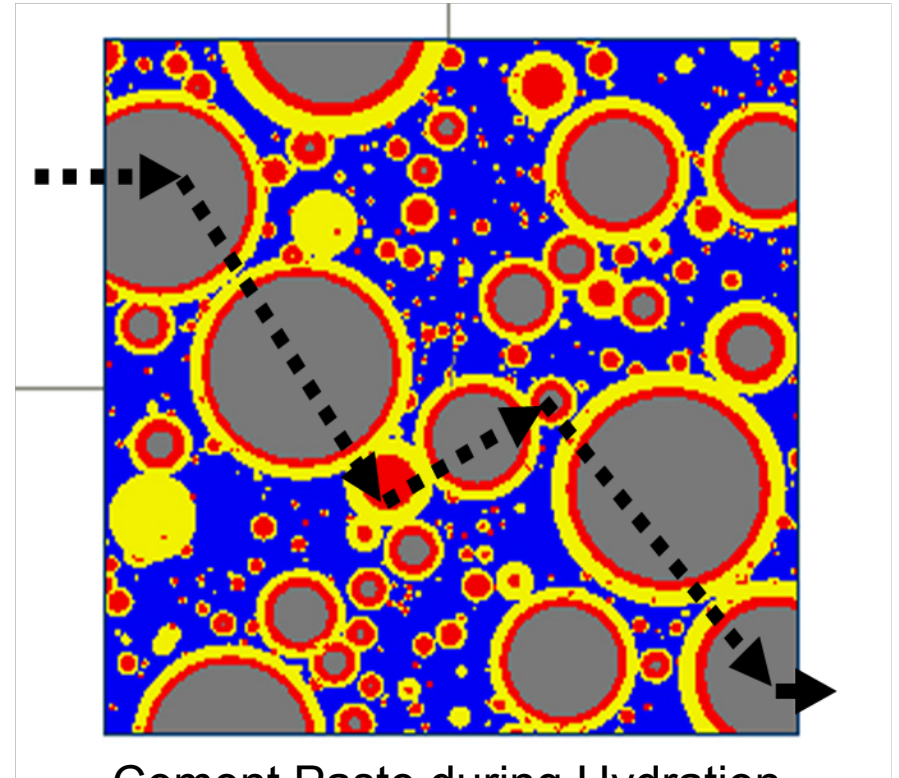




Percolation of Solid Phase



Original Cement Paste



Cement Paste during Hydration



New Materials: Photocatalysis

- A new and innovative approach shows that **photocatalytic activity may be conferred to cementitious construction materials** such as paints, mortars, concrete, roads etc.
- TiO_2 is effective in reducing pollutants such as NO_x , aromatics, ammonia, and aldehydes
- TiO_2 in combination with cementitious materials has shown a **favorable synergistic effect in the reduction of pollutants**



Photocatalysis in Cementitious Materials

- BiancoTX Millennium white cement incorporating titanium dioxide was used for the “Dives in Misericordia” church

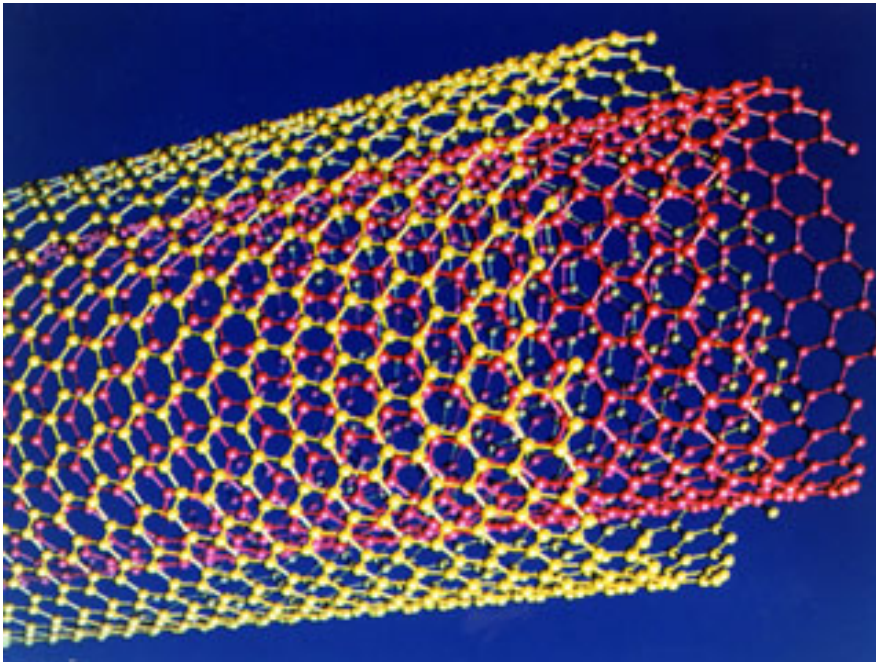


CTG Italcementi Group, Italy



New Materials: Carbon Nanotubes

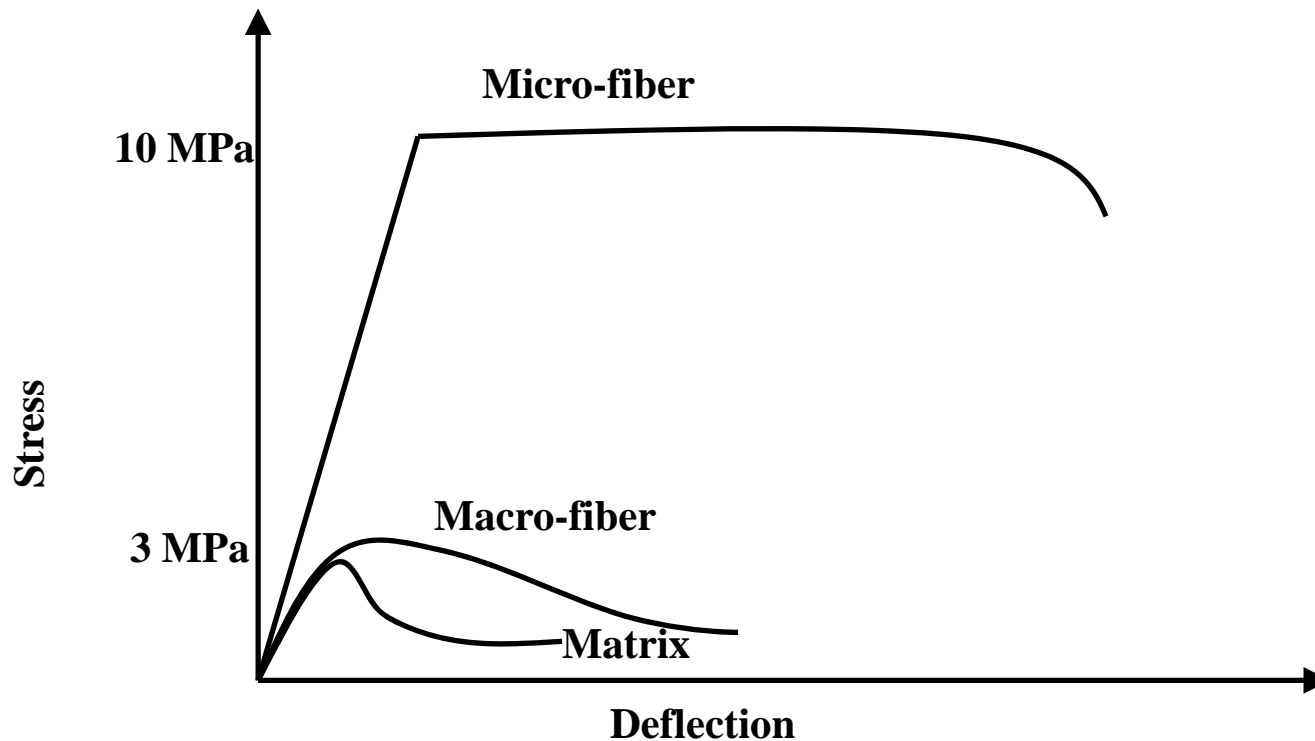
- **Extremely high tensile strengths**





Nanotechnology and FRC

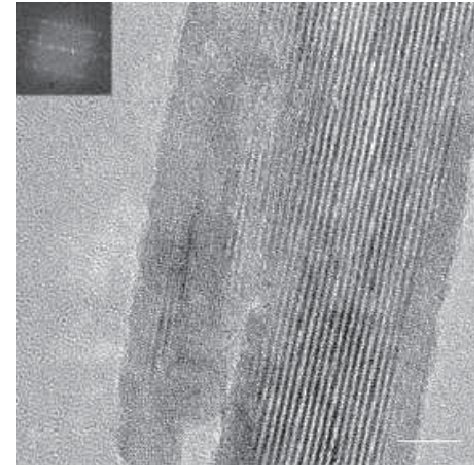
- Can we achieve superplasticity by modifying at nanoscale?





New (Old?) Materials!

- Damascus sabers contain *carbon nanotubes*, as well as *nanoscale wires of cementite*, giving them a moiré pattern (from Nov. 28 article in NY Times, photo taken by Tina Fineberg)
- Nanotubes over 400 years old!



TEM image showing nanotubes
[Reibold et. al, 2006]





Thank you!



Acknowledgements



National Science Foundation
WHERE DISCOVERIES BEGIN



U.S. Department of Transportation
**Federal Highway
Administration**



NATIONAL READY MIXED CONCRETE ASSOCIATION



The Concrete Industry's
**Strategic Development
Council**



Universidad
Complutense
Madrid



NORTHWESTERN UNIVERSITY
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